PREPARATION AND PROPERTIES OF ALUMINA DISPERSED COPPER STRIPS

by

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INDIAN INSTITUTE OF TECHNOLOGY, KANPUR

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MAY, 1987

To

My Parents

CERTIFICATE

This is to certify that the present work on "PREPARATION AND PROPERTIES OF ALUMINA DISPERSED COPPER STRIPS" has been carried out by Mr. K. Padmanabha Rao under my supervision and it has not been submitted elsewhere for a degree.

May, 1987.

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SYNOPSIS

In the present study, an attempt has been made to produce alumina dispersed copper strips by a powder metallurgy route, which consists of milling the mixtures of Cu and Al_2O_3 powder in an attritor. The preform prepared from such powders is sintered followed by densification rolling either by hot rolling or repeated cold rolling - sintering cycle.

It has been observed that making of $Cu-Al_2O_3$ strip by the powder metallurgy route "Powder Preform Making - Sintering - Repeated Cold Rolling and Resintering" does not produce satisfact strip due to cracking problem. The route "powder preform making - sintering - hot rolling" produces fully dense strip without any cracking problem.

It has been found that the mechanical properties of the $Cu-Al_2O_3$ strip depends on size and volume fraction of alumina particles, and time of attritor milling. The results obtained in this work are comparable with those produced by other techniques.

CHAPTER 1

INTRODUCTION

Modern technology continually demands improved metals which are able to withstand greater stresses, particularly at elevated temperatures reaching 0.8-0.9 T_m (melting temperature)[1]. The demand for increasingly complex requirements in electrical industries has provoked the need for electrical conductor materials with higher strength at high operating temperatures. To meet this requirement, a wide range of research efforts are expended towards the modification of existent conductor materials, changes in processing or chemical composition and the development of entirely new material systems[2]. The typical one of the last, is the oxide dispersion strengthened (ODS) copper which is developed to meet the critical demand in electrical industry. The mechanism of retention of ambient strength values at elevated temperature is briefly discussed in later section in this chapter.

In attempting to produce ODS copper, many techniques and processes were studied experimentally on pilot scale in various laboratories and research institutes. In most of the cases, it was difficult to make ODS copper on a mass scale and if so, at economical costs. To overcome this, a novel attempt can be tried to make this material by using the recent technique of mechanical alloying and powder metallurgy route to prepare the powder and strips respectively, at relatively lower costs.

1.1 Need of Dispersion Strengthening:

The requirement of retention of ambient strength values at elevated temperatures nearing 0.9 T_m, is not going to be met by metals strengthened with conventional mechanisms, whose limitations are briefly mentioned as below.[3]

Metals strengthened by strain hardening will lose much of their strength at relatively lower temperatures which are slightly more than the recrystallization temperature due to nucleation and growth of strain free grains. Metals strengthened by solid solution strengthening mechanism, will soften at temperatures approaching half the solidus temperature. More over, the intrinsic physical properties viz., electrical and thermal conductivity, are altered significantly due to distortion of solvent lattice by solute atoms which is not desirable in electrical conduction purpose. Metals strengthened by precipitation strengthening mechanism will significantly loose their ambient strength values at temperatures higher than that of prior aging treatment due to coarsening and dissolution of precipitates in the matrix. These metals will not alter the intrinsic physical properties so that these are widely adopted in common usage.

The above mentioned limitations are eliminated in dispersion strengthening mechanism, because of uniformly distributed and closely spaced with interparticle spacing of less than 1 μm size or 300-500 Å of noncoherent, nonshearable and thermally stable near spherical shaped dispersoids of size of 0.3 μm or still

less than this. Because of above fine distribution and size of dispersoids in the metal, the grain growth and plastic deformation at elevated temperature are impeded. At room temperature, the mechanical strength is improved due to a direct particle-dislocation interaction and sub-cell structure formation because of retention of stored energy. The requirements of the dispersoids are dealt with in the following section.

1.2 Requirements of the dispersoids:

Following are the requirements to be met by the dispersoids

- (i) Dispersoids should possess high hardness.
- (ii) Dispersoids must have high thermal stability at elevated temperatures.
- (iii) Dispersoids must have high chemical inertness and insolubility in the matrix of metal to impede its plastic deformation at elevated temperatures.
- (iv) Dispersoids should be cheaply available in fine particulate form at sizes of less than 0.3 μ-m.

Keeping in mind the above listed requirements, refractory materials will be the obvious choice and among them - oxides, carbides, nitrides and borides[4] are the competitive materials. Out of these, oxides are the best suitable as dispersoids due to their higher thermal stability which is because of their high negative free energy of formation of -418 KJ/mole and their

availability at comparatively lower cost. Oxides of reactive elements such as Th, Ti, Zr, Y and Al are better than that of nonreactive elements like Cu, Ni, Fe etc., because of higher thermal stability on relative scale.

1.3 General Characteristics of O.D.S. Copper:

ODS copper will retain more than 85% of its strength after 3600s exposure to temperatures upto 1273K which implies no appreciable recrystallization. Strength at elevated temperatures can be improved by using proper Thermo Mechanical Treatment (TMT) due to improved distribution of dispersoid whose agglomerates will be broken so that better interaction of dislocation and oxide particles is achieved. Because of this, the strength at room temperature is also improved.[5,6] The rate of work hardening is reduced due to uniformly distributed dispersoids in the metal, so that larger reduction per pass can be given in rolling schedule to get strips or in other words, larger amount of cold working can be given in other modes of deformation without much difficulty[3]. Since the chemical interaction between the dispersoids and the metal matrix is negligible[1] and spacing of the dispersed particles is greater than the mean free path of the electrons in copper, the electrical and thermal conductivity will only be reduced by a small fraction at the room temperature and comparable at temperatures above 573K

with pure copper. The wear resistance of ODS copper is significantly improved[8] which is an important factor for low duty electrical contact material. The fatigue resistance is also higher for ODS copper[3].

In comparison to this copper, other copper alloys like Cu-Cd, Cu-Cd-Zr and Cu-Ag will show significant softening above temperature. 623K and greater drop of electrical and thermal conductivities is observed. This trend of above property is also observed in OFHC copper at above 523K[3].

1.4 Applications of ODS Copper:

ODS copper has wide market acceptance in several applications, and design engineers are continually developing new applications. The major application of this copper are listed as follows:[3]

(i) For resistance welding electrodes - to over-come the difficulty of tip deformation (called mush-rooming) rates and sticking problem against galvanised steel sheets in automobile industry, so that productivity has improved.

(ii) For lead wires in incandescent lamps and in leads for discrete electronic components such as diodes in electrical and electronic manufacturing Industry.

(iii) Commutators for helicopter starter motors and in car radiators because of better heat transfer properties.

(iv) Relay blades and contact supports to increase current carrying capacity and to improve service life in electric circuits.

(v) Miscellaneous usage for continuous casting molds for steels, side dam blocks for hazlett casting machine for zinc, GMAW tips, seam welding wheels, high current welding cables, microwave tube components, electrical connectors, transformer switching terminals, lead wires for heating elements and thermocouples, high temperature magnet wire, stud bases for powder transistors and rectifiers[4].

In sheet and strip form, ODS copper has got structural and electrical contact applications.

1.5 Mechanism and Models of Dispersion Strengthening in ODS Copp

According to Fisher et al.[9], strengthening effect is closely related to the fine size of dispersoid and interparticle spacing (λ) between them. The flow stress increment at high strains, is proportional to radius of dispersed phase. In another model[10] proposed by Ansell, the flow stress increment is due to the Orowan mechanism because of finer interparticle spacing (λ) of less than 1 μm (preferably 500 A°) and finer size of 150-300 A° of nonshearable dispersoid particles (oxide particles) to restrict the movement of dislocations which have to bow out from dispersoids and results in high energy requiremen to do so for dislocation. Moreover, such finely and uniformly

distributed nonshearable oxide particles will impede the grain boundary sliding at elevated temperature which results in retention of the ambient strength values to a considerable extent. This model satisfies the validity of mathematical equation of Orowan mechanism to the ODS copper system which is started as follows:

$$\Delta\sigma = \frac{Gb}{\lambda}$$

where

$\Delta\sigma$ = improvement in flow stress, MPa

G = shear modulus, MPa

b = burger's vector, A°

λ = interparticle spacing, A°

Even though the above two models are applicable to ODS copper, a more rigorous analysis by Preston et al[11] which gives the correlation of stored energy due to plastic deformation and improvement in flow stress. This leads to further understanding of indirect effect of dispersoid on the metal matrix to increased store energy so that finer dislocation cell structures form and improve the strength properties. The empirical relation for energy stored per unit volume of ODS copper is as follows:

$$E = \frac{n\gamma}{r} \left(\frac{3f}{4\pi}\right)^{1/3} - \left(\frac{3f}{4d}\right)$$

where

r = particle radius

f = volume fraction of dispersed phase

d = distance between particles

n = number of subboundary planes passing through the particles

γ = specific subboundary energy.

Also, this model relates the strength of ODS copper to the degree of dispersion of oxide particles indirectly through its effect on the ability of the structure to retain strain energy from plastic deformation. Satisfactory correlation is also obtained for both ambient and elevated yield and creep rupture strengths. According to above models, the optimum mechanical properties can be expected with oxide content of 3-5 vol.% when particle size is 30-50A°. Because the interface between oxide particles and copper matrix is incoherent, it can act as a sink for dislocations and improve the strength values.

1.6 Requirement of Powder Metallurgy Route to Prepare ODS Copper Strips:

Conventional melting and casting techniques are unsuccessful to be applied for production of ODS copper because of high interfacial energy between the molten metal and oxide particles, which leads to flocculation. Besides this, segregation in melt also occurs due to greater disparity in density of molten metal

and oxide particles which is difficult to control solidification process to achieve uniform and fine dispersion of oxide particles(3).

Powder Metallurgy (P/M) routes for manufacture of ODS copper overcome the above drawbacks and infact, this is the only alternative process for ODS copper. The high cost of powder can be balanced to some extent by lower wastage of material. On the whole, ODS copper is costlier than other copper alloys, but its property advantages will outweigh its higher cost by reducing the required cross sectional area for current passage(3).

1.7 Methods for Making Oxide Dispersed Copper Powder:

There are various methods for producing oxide dispersed copper powder which are briefly outlined with their limitations.

Coprecipitation(12) from a water solution containing copper and reactive element like Al as hydroxides can be made by the addition of NaOH. After precipitation, the powder is oxidised in air and reduced at a suitable temperature in H_2 so that copper is reduced from less stable copper oxide when compared with oxide of reactive element like Al. Finally, the resultant powder consists of Cu and reactive element's oxide of very fine size ranges from 50-150 A°. Even though the distribution of dispersoid oxide is good, the difficulty to control the process in this method obviates its choice for commercial application. Moreover, the cost of this process is high.

Spray drying followed by selective reduction technique[13,1 involves preparation of the solution containing copper acetate and thorium nitrate particles and spraying the solution on suitable substrate and drying followed by subsequent oxidation at 500°C. After this, the powder is subjected to hydrogen reduction to reduce cuprous oxide to copper. Because of the number of the steps involved this process is difficult to control.

Reversed gel precipitation[14] is a process similar to coprecipitation. The main differenteis that the solution contains an organic compound, e.g. a polysaccharide or rubber, which controls the viscosity and forms a complex together with the metal hydroxide. This means that there is a copious nucleation resulting in avery fine particle size. This process also is costly.

Electrodeposition[8] from an acid copper sulphate solution containing Al_2O_3 particles results in incorporation of the Al_2O_3 particles in the growing copper dendrites. A high current density gives a steep concentration gradient which results in break up of the growing copper dendrites and the particles settle at the bottom to form the desired Cu-Al_2O_3 powder. This process is controlled by the current density, the suspended Al_2O_3 content, the Al_2O_3 - particle size and the chemical composition of the electrolyte. This process is of limited use due to higher cost of production.

Internal oxidation[3,4,16] is a method for producing a high quality ODS copper powder. The dilute solid solution of Cu-Al melt is prepared and atomized to powder by using an inert gas. After atomization, the powder is oxidized in a controlled atmosphere, where the oxygen potential is too low for the formation of Cu_2O, but high enough to form Al_2O_3. This process was developed on a commercial scale and now is a proprietory process of SCM metal products, USA[4]. Still, the cost of powder is comparatively higher.

Mechanical mixing[2,8,17-19] is the more simple and cheaper way to produce ODS copper powder on comparative scale. The volume fraction of oxides can be easily controlled because no chemical processing steps are involved and the equipment needed is simple and cheap. The quality of the distribution of oxide particles largely depends on finer copper powder with dendritic shape so that larger surface sites on copper powder will be available for uniform distribution of oxide particles. Wet milling is preferred to attain better distribution of oxide particles in copper. Seggregation and coagulation of the dispersoid phase cannot be avoided in this process which results the addition of more oxide particles than is required so that optimum properties cannot be achieved. Typically, the copper powder's average size should be less than 5μm and that of oxide will be atleast less than 30-50 times of copper powder. This requirement of size and shape of powder is

restricting the wide adoptability of this method for making oxide dispersed copper powder.

Except mechanical mixing, all the above methods are costlier to make ODS copper and limit the acceptance of this copper in commercial applications. Because of larger time of milling in mechanical mixing, typically 20-30 hours and above mentioned problems, a more competitive method is needed to make ODS copper. Recently, a new technique called "Mechanical Alloying which was originally developed for preparation of ODS Ni base superalloy powder and extended to stainless steel powder and currently for making Al-Li and Al - transition element rapidly solidified alloy powders[20], can be tried to make ODS copper. Moreover, the flexibility in mechanical alloying technique relieves the process restriction on chemistry of matrix metal into which dispersoids are incorporated. In case of copper alloys like Cu-Cd and Cu-Cd-Cr systems, it was reported that the distribution of oxide particles in the alloy matrix was difficult due to seggregation of oxide particles caused by cadmium present in the alloy[2]. To overcome this difficulty, mechanical alloying can be tried to distribute uniformly oxide particles by charging individual powders so that true alloying between Cu and Cd takes place on atomic scale in solid state. Even though, no solid state alloying takes place in Cu-Al_2O_3 powder because of insolubility of Al_2O_3 in copper, the term Mechanical Alloying is used in present investigation due to its familiarity in powder metallurgy area. Actually, fine uniform distribution

of Al_2O_3 particles as dispersoids in copper powder occurs during attributor milling in mechanical alloying operation. Details of mechanical alloying technique are discussed briefly in next section.

1.8 Mechanical Alloying:

Mechanical Alloying was developed as a means of overcoming the disadvantages of mebhanical mixing without encountering the difficulties associated with ultra fine powder requirement, to accelerate the formation of Cu-oxide composite powder and to eliminate the dependency of final Cu-Al_2O_3 powder on initial copper powder size. Mechanical alloying results a controlled homogeneous composite structure in copper powder by competitive actions of cold welding and fracturing of different sizes of particles. If the two components are insoluble in the solid state, then a fine dispersion of one in other is achieved by this technique[21,22]. This feature was utilised successfully to develop ODS nickel base superalloy powder, stainless steel powder and aluminium alloys like Al-Mg or Al-Mg-Li or Al-Li or Al-transition elements like Fe, Ti and V etc alloys[20,23-26].

Mechanical alloying was also tried for Cu-Pb system[27]. Recently, it was established that mechanical alloying gives true alloying on atomic scale for both ductile constituent systems like amorphous Ni-Nb[28], Ni-Cr[21], Cu-Zn[29] to get ordered Beta phase and for brittle constituent system of Si

and Ge[30]. Besides these applications, mechanical alloying has also been used to produce superconductor materials by making multiphase composite powders like ZrO_2 coated with Tungsten and then distribute in Nickel system[21].

In general, milling step takes appreciable time in mechanical alloying so that carefully controlled thermomechanical processing is frequently needed and the cost involved does not justify the application of this technique to normal alloy systems made by melting-costing route. Mechanical alloying is generally applied for incompatible constituent systems like metastable phases, incongruent melting intermetallics, cermets etc.[20]

Mechanical Alloying is carried out in a high energy rate Ball mill, called as attritor mill, whose schematic diagram is shown in Fig. 1.1. This attritor mill consists of a vertical water cooled double stainless steel shell drum with a series of motor driven impellers through a shaft so that the grinding media of either AISI 52100 steel balls or Tungsten carbide balls in the drum are rapidly agitated. The grinding rate is more than 10 times higher than that of a conventional Ball mill the drum itself is rotated. These attritor mills are batch type, continuous and recirculation types, out of these, the last one is the best for mass production. The agitation in attritor mill by the impellers causes a differential movement between the balls and the material being milled to provide a substantially higher degree of surface contact for composite

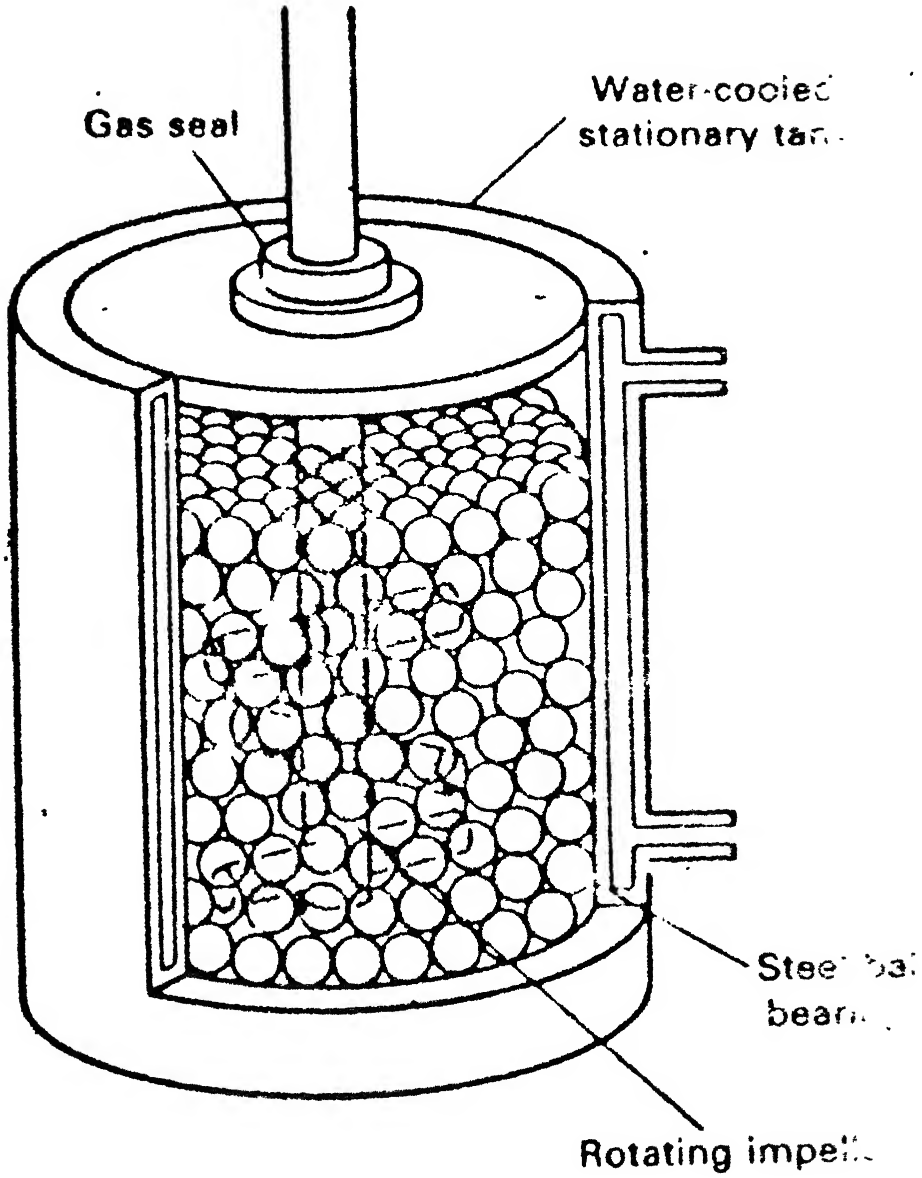

Fig. 1.1   Schematic diagram of attritor mill

powder formation. Milling action is accomplished by impact and shear forces[31] in attritor mills. The rotating charge of balls and milling product form a vortex at the upper end of the stirring shaft, into which the milling product and balls are drawn. The milling product is further impacted by balls travelling in various trajectories that collide within the dilated charge of grinding medium and powder.

The oxidation of powder in attritor mill is minimised by using either inert gas atmosphere of N_2 or organic liquid like acetone or methanol which is cheaper than N_2. The attritor mill is generally rotated at 140 rpm and ratio of grinding media to powder is maintained between 20:1 and 30:1. After attritor milling, it is advisable to subject the oxide-dispersed powder for stress relieving and reduction treatment in H_2 atmosphere at 850°C for 900s time.

1.8.1 Stages and Mechanism of Mechanical Alloying:

Mechanical alloying can be divided into 5 stages[33] according to Benjamin et al, which are listed as follows:

(i) early or initial stage where fracturing is a predominant phenomena.

(ii) period of welding predominance.

(iii) period of equiaxed particle formation.

(iv) start of random welding orientation.

(v) steady state processing which occurs usually after 5,400s time.

The homogenity of composite powder is logarithmic function of attrior milling time so that rate of structural refinement is dependent upon the rate of mechanical energy input to process and the work hardening rate of material being processed. After attaining the balance between welding and fracturing, little change in particle size distribution will occurs, but the structur of the particles is steadily refined to such an extent that the layered structure in the powder cannot be resolved by optical microscopy.

Typically, the duration of mechanical alloying is usually more than 3,200s to attain satisfactory refinement in ductile constituent system.

1.9 Preparation of ODS Copper Strip via P/M Routes:

After making oxide dispersed copper powder by suitable method, the strips can be made by vacuum sealing the powder in a copper container and isostatically compacting and then hot extruded into a bar form from which strips are made by rolling[4]. Alternatively, the powder can be compacted in a die and sintered, after this, it is subjected to rolling schedule[34]. A more complicated processing consisting of Isostatic pressing at 350 MPa, sintering at 1073K for 36,000s (12 hours) and hot press forged to increase density and ductility of material has also been reported. After this, hot rolling is used as a final step with 10% reduction per pass on average[13]. Because of above costly

and complicated processing steps, more competitive methods for producing strips by other means which have been extensively reviewed by Dube(35), can be applied for ODS copper and these are discussed in the subsequent section.

1.10 Alternative P/M Routes for making ODS Copper Strips:

The alternative P/M route may comprise of the following basic processing steps(35) which are illustrated in Figure 1.2.

(1) Making green strip by direct powder rolling or by bonded powder rolling method.

(2) Sintering of green strip.

(3) Densification by either hot rolling in one single step or repeated cold rolling and resintering schedule.

(4) Strengthening the fully densified strip by subjecting it to cold rolling and annealing treatment.

The above steps are discussed in detail in following subsections.

1.10.1 Preparation of the Green Strip:

The green strip which can be defined as a mechanically bonded metal powder formed into a strip which is porous and weak. This green strip can be made in two ways which are briefly outlined as follows.

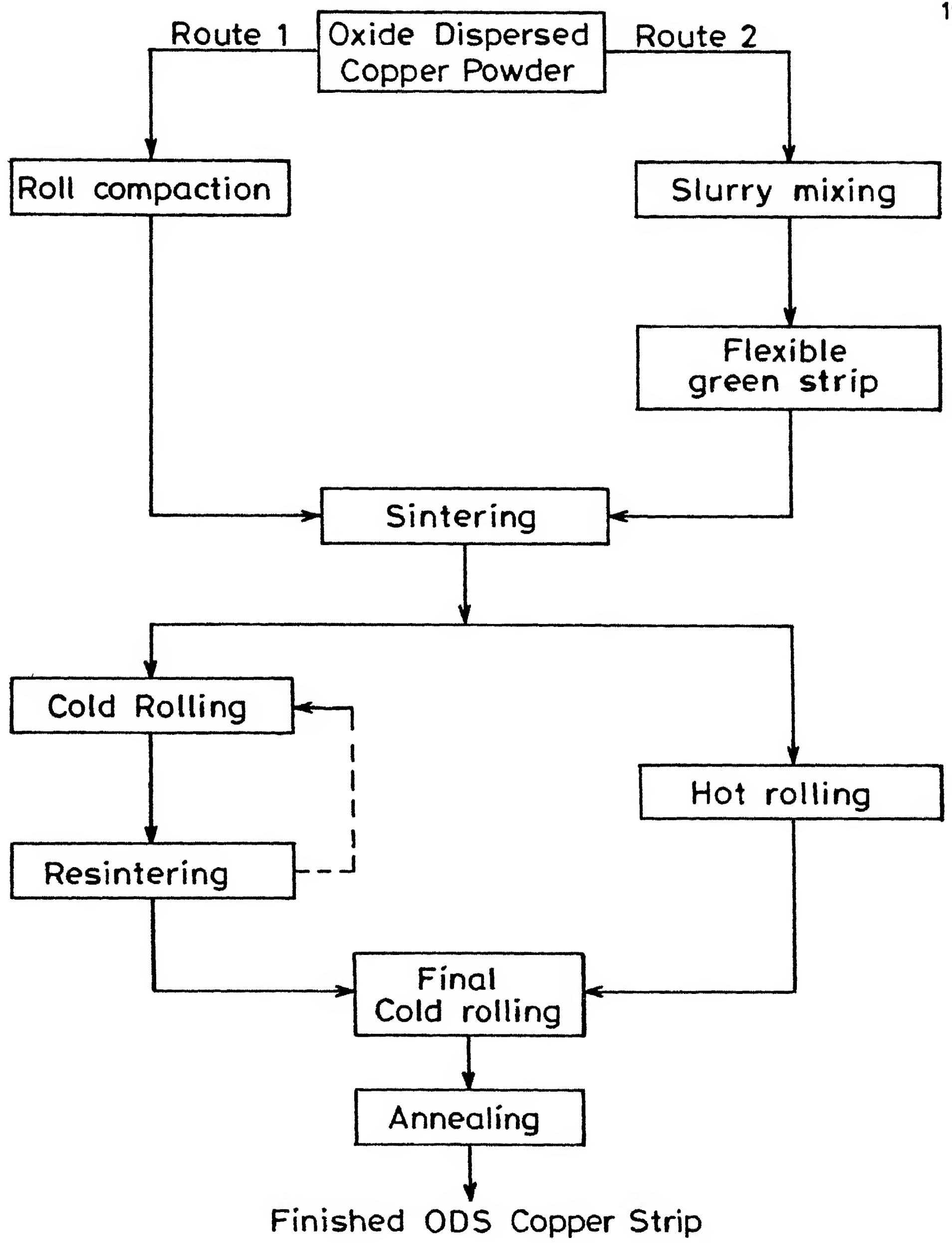

Fig. 1.1 Schematic flow diagram of P/M routes for ODS copper strip.

1.10.1.1 Direct Rolling of Powder:

Direct rolling of oxide dispersed copper powder is simple to perform for relatively large and irregular powder, but can be very difficult to do for finer powder due to fluidization of the powder. Moreover, in this method, it is difficult to control the distribution of density along the width of strip and maximum thickness of strip to be produced is limited[36]. Forced powder feeding is preferred in this method. In general, direct powder rolling is difficult to carry out for fine powder.

1.10.1.2 Bonded Powder Rolling:

The problems associated with direct powder rolling method are overcome by this method. The green strip is prepared by making viscous slurry of dispersed copper powder with suitable binder, plasticizer and solvent, then pour the slurry on a suitable substrate and dry it to get porous green strip after applying suitable nonadherent organic coating on the substrate. The advantage of this method is that the thickness of the strip, is independent of powder characteristics and mill parameters. The density of green strip depends upon the powder size, solid liquid ratio in the slurry, viscosity of the slurry etc. The green strip after drying, contracts to some extent depending upon the apparent density of the slurry[36]. So, this method is more suitable because conventional rolling mill can be used for densification and making the strip without the need of a special powder rolling mill. Moreover, the steps in preparation

of green strips are simple to carryout.

1.10.2 Sintering:

Sintering is done to improve the strength of green strip. To prevent oxidation of the porous green strip and to remove the impurities such as surface oxide films, a suitable reducing atmosphere like H_2 is used in furnace. Sintering is usually carried out on flat green strip in horizontal furnace with high temperature. Low time cycle to improve the productivity due to the fact that sintering time can be reduced to 1800s when sintering temperature approaches 0.7 to 0.85 T_m (melting temperature of copper). This happens, because of accelerated bonding between the particles which improves the strength[37]. The strip after sintering is relatively porous but which adequate strength for handling.

1.10.3 Densification Rolling of Sintered Cu-Oxide Dispersed Strip:

The densification of sintered oxide dispersed copper strip is done to get a fully dense strip and can be carried out by either hot rolling in one single pass or by repeated cold rolling and resintering cycle. The details of these two methods are discussed below.

1.10.3.1 Hot Rolling:

This is a favourable method to achieve 100% densification in the sintered strip because it can be achieved in one pass. Moreover, it is possible to hot roll the sintered strip directly

into a dense strip from the sintering furnace so that productivity is improved. Generally, the amount of thickness deformation required to produce a fully dense strip depends on the initial porosity and is always greater than that of the theoretically required because of resultant elongation of strip by rolling[38]. The fully dense hot rolled strips can be cooled in a protective atmosphere to prevent oxidation[39] or after partial cooling in protective atmosphere. The strip can be water cooled followed by pickling to remove surface films[40].

1.10.3.2 <u>Repeated Cold Rolling and Resintering Cycle:</u>

Fully dense strip can be made from sintered strip by this method which requires approximately 70% total reduction with intermediate resintering for short duration of 900s at 1123K[41].

However, the initial thickness reduction is limited by 20% owing to the presence of highly dispersed porosity which makes the strip to crack easily[42]. After first pass, greater % reduction can be given in subsequent passes.

Generally, several cold rolling and resintering cycles are required to achieve fully dense strip in the cold rolling route. For this reason, hot rolling is more advantageous.

1.10.4 <u>Final Cold Rolling and Annealing:</u>

This is to improve optimum mechanical and structural properties in addition to superior surface finish. Hot rolled

O/M metal strip will have poor surface finish due to oxide film formation. It is necessary to pickle this strip before this final treatment. This treatment can be combined with repeated cold rolling and resintering cycle densification method[37]. The annealing temperature and time are similar to strips made by conventional route after full densification of powdered metal strip.

1.11 Aim of the Present Investigation:

The objectives of the present investigation were:

i) To prepare copper-alumina composite powder by mechanical alloying method.

ii) To prepare fully dense copper-alumina strip from the above powder.

iii) To optimise the rolling schedule to make fully dense strip.

iv) To evaluate the mechanical properties of the strip produced and to compare it with those obtained by other researchers.

CHAPTER 2

RAW MATERIALS AND EXPERIMENTAL PROCEDURE

2.1 Raw Materials:

2.1.1 Copper Powder:

Copper powder was produced by gas atomization and supplied by green pack industries Inc., USA. This powder was 99.51% pure and had an apparent density of 2.83 Mg/m^3. The standard Hall flowmeter rating of this powder was 34 seconds per 50 grams. The size distribution of powder is reported in Table I. The average size of this powder was 12 μm, as stated by the manufacturer.

2.1.2 Alumina Powder:

Alumina was chosen as oxide dispersoid because of its relative cheapness. Two grades of different particle size of α-and γ-Al_2O_3 powders were used and supplied by Buehler's Ltd., USA. The characteristics of these powders are gives as below:

(i) α-Al_2O_3 with hexagonal crystal structure	Linde A grade Apparent density: 0.27 Mg/m^3 Average particle size: 0.3 μm
(ii) γ-Al_2O_3 with cubic Crystal structure	Linde C grade Apparent density: 0.13 Mg/m^3 Average particle size: 0.05 μm.

TABLE I : Size Distribution of Copper Powder used in Present work

Mesh number	wt %
+100	0.2
+150	4.2
+200	7.5
+250	5.3
+325	18.9
-325	63.9

2.1.3 Methanol:

Electronic grade methanol, supplied by S.R. Chemical Lab., India, was used to control the oxidation of powder in the attritor during mechanical alloying operation.

2.1.4 Binder:

Reagent grade methyl cellulose was used as binder. This was necessary to form a homogeneous slurry of the powder with sufficient viscosity.

2.1.5 Plasticizer:

Methyl cellulose, when used as a binder, produced enough flexibility in the green strip after drying. Glycerine was used to produce plasticizing effect in a methyl cellulose water system. Reagent grade glycerine was used as plasticizer in the present investigation.

2.1.6 Acetone:

Acetone of electronic grade was used for cleaning the grinding media used in attritor between the trials.

2.1.7 Tungsten Carbide Balls:

Tungsten carbide balls were used as grinding media in the attritor. The weight of each ball was 4.4 gm with the shape comprising central cylindrical portion having diameter of 7.8 mm and height of 2 mm and hemispherical shape on both sides of the cylindrical position with diameter of 7.6 mm and the total height of the ball is 4.8 mm. This shape was ideal for good

grinding action in attritor mills.

2.1.8 Gases:

Nitrogen gas was used to purge out the oxygen present inside the furnace before passing hydrogen at high temperature. Hydrogen was used to protect the green strip from oxidation and also to reduce the oxides present in the sample. IOLAR-1 grade hydrogen and standard nitrogen supplied in cylinders by Indian Oxygen Limited were used.

2.2 Experimental Procedure

2.2.1 Preparation of Alumina Dispersed Copper Powder:

As mentioned earlier, oxide dispersed copper powder was prepared using Al_2O_3 as dispersoid by mechanical alloying technique and was carried out in a high energy rate attritor mill supplied by Torrance and Company, U.K. An accurately weighed 0.22×10^{-3} Mg charge of copper powder with volume fractions of 3%, 6% or 8% of Al_2O_3 was mixed manually for 1 hour by using mortar and pestle to ensure rough mixing of copper and alumina powders. This hand mixed Cu-Al_2O_3 powder was charged into the attritor which was filled to nearly half of its volume by Tungsten carbide balls used as grinding media. After the powder addition, grinding media was further introduced so that slightly more than half of the volume of double jacketed water cooled stainless steel drum of attritor was filled. Then, the mill was run initially at slow speed and methanol was added to prevent the oxidation of the Cu-Al_2O_3 powder during mechanical alloying

action. After the addition of methanol, the drum was closed tightly by a stainless steel lid and attritor was run at a speed of 140 r.p.m. for different periods of time, i.e., 7200, 14400 and 28800 seconds. After completion of mechanical alloying, the powder was drined and taken out from bottom of the drum and separated from methanol after settling of powder. Used methanol is again recirculated for 3 times to cleans the grinding media for carrying out trials for same volume fraction material.

Before starting trials for different volume fraction materials the drum of attritor and grinding media were thoroughly cleaned with acetone. The separated powder from methanol was dried at temperature of 75-100°C for 6 hours. Typically apparent density of Cu-Al_2O_3 powder was found as 0.4 Mg/m^3.

2.2.2 Preparation of Green Copper-Al_2O_3 Strip:

Cu-Al_2O_3 powder and binder were weighed accurately and blended manually. This mixture was transferred to 400 ml beaker. Water was mixed with glycerine in a 100 ml beaker separately. Water-glycerine mixture was slowly added to Cu-Al_2O_3 powder by using a direct power deriven stirrer, supplied by Toshiba Electric Company, India. The slurry thus formed contained some air bubbles which resulted into small blow holes in the green strip . Care was taken to minimize the trapping of air bubbles by using a lower speed of mixing. The composition of the slurry is shown in Table 2.2.

TABLE II : **Composition of the Slurry made in the Present Work**

Constituent	Weight %
$Cu-Al_2O_3$ powder	61.2
Methyl cellulose	1.2
Glycerine	2.4 (2 ml)
Water	55.5

The free flowing slurry was poured into a rectangular mould of dimension 100x75x10 mm. Before pouring the slurry the mould surface was coated with oleic acid which act as a releasing agent. The cast slurry was dried on a hot plate and subsequently allowed for further drying in electric oven maintained at 100°C for 8 hours. The apparent density of green $Cu-Al_2O_3$ strip was 1.0 Mg/m^3. The dried green strip was pressed between flat platens on a hydraulic press using 130 MPa pressure. The compacted strip was found to have fragile edges because of the constraints from sides, which were removed. The apparent density of the pressed strip was about 4.2 Mg/m^3.

2.2.3 Preparation of Green Strip by Die Compaction Technique:

Mechanically alloyed $Cu-Al_2O_3$ powder was also compacted into a rectangular shape of size 40mm x 69 mmx 4.5 mm by using tool steel die and punches. The weight of powder used to produce above compact was 65 grams. The apparent density of compact was 4.4 - 4.7 Mg/m^3 which is typically 50-55% of theoretical density of $Cu-Al_2O_3$ fully dense strip. The pressure applied for the compaction was 150 MPa.

2.2.4 Sintering of the Green Strip:

The sintering furnace used in the present investigation is shown in Fig. 2.1. The chamber of the furnace was 750 mm long and 100 mm in internal diameter. It was made up of Inconel Tube. The chamber was closed at one end. The open end of the furnaces had a 200mm long cooling chamber where the sintered $Cu-Al_2O_3$ strips or compacts were cooled to 70°C under hydrogen

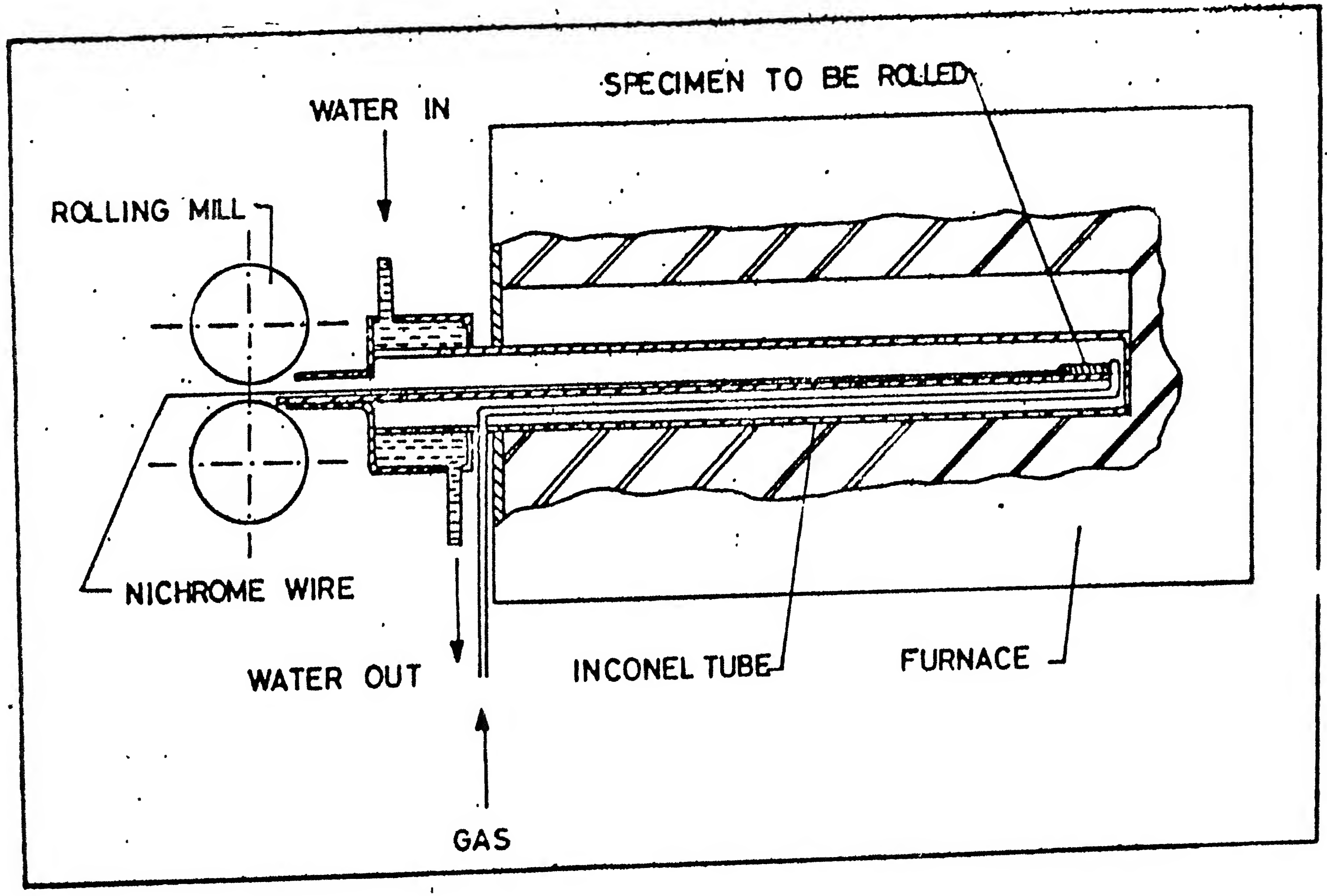

Fig. 2.1 Hot rolling arrangement.

atmosphere prior to taking out from the furnace. Gases were introduced in the chamber through a 16 mm internal diameter stainless steel tube passing through the open end of the chamber and were released near its closed end. The unused reducing gas was burnt at the exit.

The standard procedure for sintering was that, the chamber was flushed with Nitrogen for about 5 minutes before introducing nitrogen, the furnace was maintained at the required temperature. The green strip or compact, placed in a perforated inconel tray, was then pushed into the hot zone of the furnace. After the required sintering time, the tray was removed from the hot zone and placed at the cooling zone for 30 minutes before taking it out. In the present investigation, the green strip was sintered at 1123K for 1800 seconds. This temperature was selected because it is the maximum sintering temperature at which commercial production is carried out at minimum maintenance cost.

2.2.5 Densification Rolling of the Sintered Strip:

Densification of the $Cu\text{-}Al_2O_3$ sintered strip or compact was carried out by two different routes:

(a) Cold rolling-resintering cycle,

(b) Hot rolling.

2.2.5.1 Cold Rolling - Resintering Cycle:

The sintered and cooled strip was cold rolled on a two high laboratory rolling mill having 135 mm diameter rolls and

rotating at a speed of 55 rpm. In order to study, he cold rolling behaviour of the sintered strip, the strips were rolled to various thickness deformation, viz. 5, 10, 20 and 30 percent. It was found that the strip can not be cold rolled without rupture beyond 10 percent thickness reduction. Even, after subjecting it to annealing treatment at 1123K for 1800 seconds after two passes of cold rolling , it was also observed the lateral and edge cracks are unavoidable. The same observations were made for sintered die compact one also.

2.2.5.2 Hot Rolling:

The schematic sketch of the reheating furnace and hot rolling operation is given in Figure 2.1. The reheating and hot rolling was done in hydrogen atmosphere to prevent oxidation of the strip or compact during heating and also to reduce the surface oxides which formed during storage. One end of the reheating furnace was closed, while the other end had a zone projecting outside the furnace. The reheating chamber contained a flat plate of inconel as a base for the strip. The sintered strip or compact was preheated to 1123K for 1800 seconds prior to hot rolling. The hot rolling was done on a 2-high mill having 135 mm diameter rolls rotating at a speed of 55 rpm. The standard procedure for hot rolling was as follows:

(a) A small hole of 1 mm diameter was drilled near one edge of the porous strip and a twin nichrome wire was attached to it.

(b) The porous strip tied with nichrome wire was placed on an inconel flat plate and introduced into the hot zone of the preheating furnace.

(c) The preheating furnace was moved to front side of the rolling mill, so that the extended exit was very close to the nip of rolls.

(d) The roll gap was adjusted to the required level and then the heated $Cu-Al_2O_3$ strip or compact was pulled winto the rotating rolls from the hot zone with the help of the attached wire.

(e) The strips coming out of the mill were cooled in a bed of graphite powder for 900 seconds.

The hot rolled strips were annealed at 673K for 3600 seconds in nitrogen atmosphere to remove the work hardening introduced on the surface of the strip due to chilling caused by the relatively cold rolls. This chilling effect is significant when $Cu-Al_2O_3$ preform or strip is about 2 mm thick and the operation can be classified more accurately as warm working.

2.2.6 Cold Rolling and Annealing:

The fully dense hot rolled strips were cold rolled to various thickness reduction, viz., to 50% and 90% without any intermediate annealing. It was observed that rolling ability of $Cu-Al_2O_3$ composite strip was good because 20% reduction per pass was given.

The final annealing was done without any difficulty at 673K for 3600 seconds in nitrogen atmosphere. For comparison, pure copper powder was also subjected to the same attritor milling, sintering, rolling and annealing cycles as for $Cu-Al_2O_3$ strips.

2.3 Methods of Testing

2.3.1 Density:

The density of the porous strip or compact was measured by weight and dimension method. The density of the fully dense strip was measured by using Archimedes principle.

2.3.2 Mechanical Properties:

Yield strength, ultimate tensile strength and % elongation were determined by a universal testing machine Instron 1150. The testing was done at both room temperature and elevated temperature viz. 923K and samples were strained at a rate of 0.5mm/minute. Because of the shortage of material, the size of the specimen used for mechanical testing was not according to the BS 18 specification. But the geometry of the specimen, as shown in Fig. 2.2 was maintained according to the standard specification. A minimum of three specimens were tested in all the cases.

Elevated temperature tensile tensing was carried out by using the same tensile testing samples with slight modification of

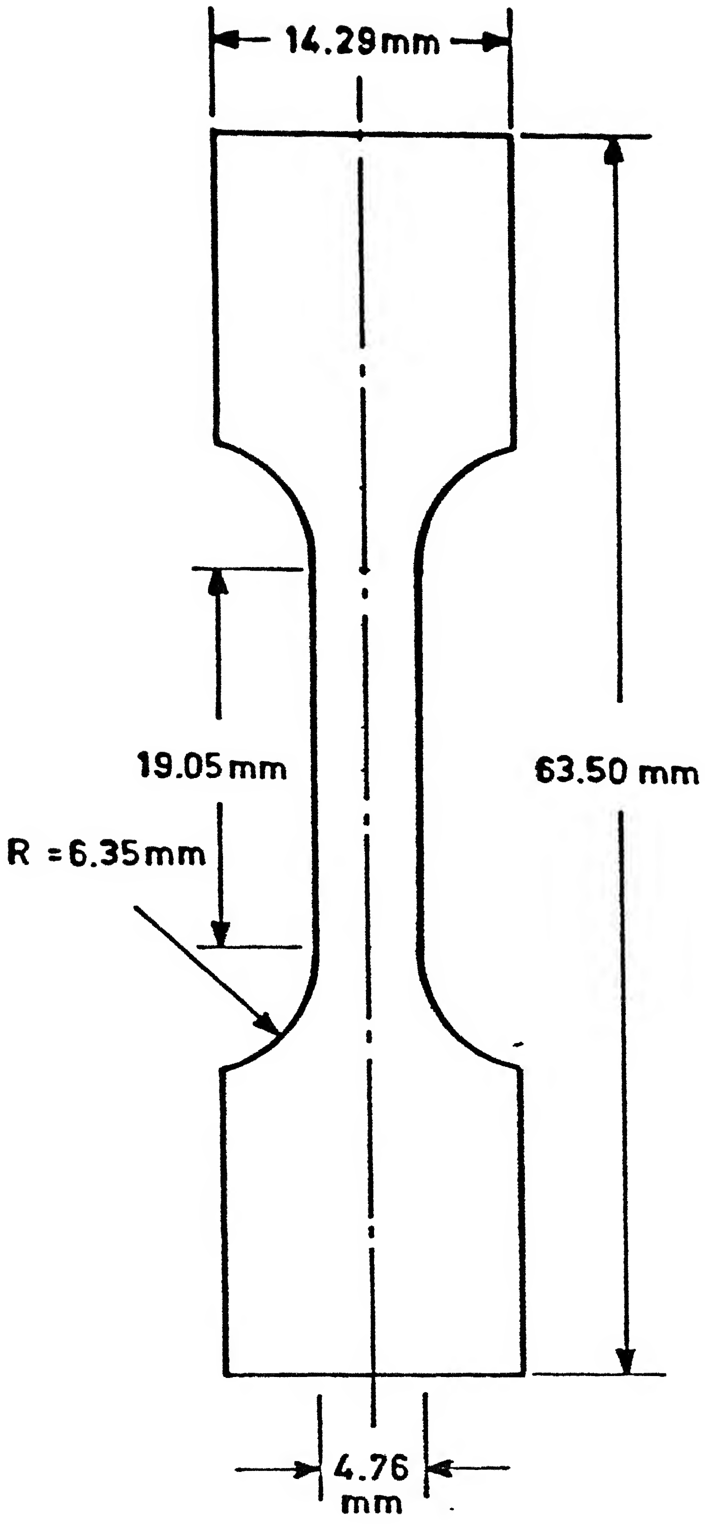

Fig Tensile test specimen.

punching of 5 mm diameter hole at the centre of shoe portion with the help of hand operated punching machine. The furnace used to heat the sample was a tubular electric resistance type with Kanthal wire as heating element and has ceramic tube (mullite type) of 40 m diameter. This test was carried out on same Instron machine with special attachment facility.

2.3.3 Creep-and Stress-Rupture Tests:

An attempt was made to perform creep test by using same type of sample meant for the above test and was carried on Satec system Inc., USA machine with a lower ratio of 16:1 at temperature 650°C. Stress rupture test was also tried.

2.3.4 Annealing Behaviour:

This was carried out by subjecting the cold rolled Cu-Al_2O_3 samples to annealing treatment for 3600 seconds at 473K, 673K, 873K, 1073K and 1273K temperature. After this, the hardness values are found out by using Leitz microhardness tester because of thinness of the samples involved which is typically of 0.25 mm for 50% cold rolled and 0.06 mm for 90% cold rolled. The indentations under load of 50 gms. are observed at 500 X magnification in the microhardness tester.

2.3.5 Optical Metallography:

The tendency of softening trend of Cu-Al_2O_3 strip was tried to correlate with microstructure by this optical metallography. The mounting of samples for metallography was

carried out by using araldite resin CY 212 and Hardener HY 951 mixture in the ratio of 10:1 by weight and subsequent curing at room temperature. The standard polishing procedure was adopted with 1 μm and 0.3 μm Al_2O_3 powder for fine grinding purpose.

The etchant used was potassium dichromate followed by ferric chloride for obtaining good contrast.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Mechanically Alloyed Cu-Al_2O_3 Powder

Alumina Dispersed Copper (Cu-Al_2O_3) powder was produced in attritor mill by Mechanical Alloying Technique. The volume fraction of alumina in copper was varied from 3% to 8% and milling operation was carried out for 7,200s, 14,400s and 28,800s. It was observed that Cu-Al_2O_3 powder was not free flowing. Typically, the attritor milled Cu-Al_2O_3 powder had apparent density of 0.4 M/m^3. Moreover, this Cu-Al_2O_3 powder was very fine and it was difficult to handle the powder.

3.1.1 Effect of Powder Characteristics on Size Distribution:

Particle size distribution of attritor milled powder depends on the characteristics of powder being used which can be seen in Fig. 3.1 and Table 3.1 for pure copper and Cu-3vol % Al_2O_3 (0.3μm size). The presence of Al_2O_3 in copper reduces the ductility of copper resulting in refiner particles in comparison with pure copper.

3.1.2 Effect of Time of Attritor Milling on Size Distribution:

Size distribution of attritor milled Cu-Al_2O_3 powders for different periods of time is presented in Fig. 3.2 and Table 3.2. It can be found that as the time of attitor milling

TABLE 3.1 : Particle size distribution of attritor milled pure copper and Cu-3vol.% Al_2O_3 (0.3 m size) powder determined by Coulter counter method

	Copper powder		$Cu-Al_2O_3$ powder	
Average particle dia.(m)	Weight percentage above corresponding size	Cumulative wt.percentage	Weight percentage	Cum. weight percentage
26.5	6.36	6.36	0	0
21.1	6.36	12.72	5.75	5.75
16.7	3.97	16.69	11.5	17.25
13.3	19.07	35.78	8.3	25.88
10.5	6.55	42.33	3.59	29.47
8.4	1.09	43.42	4.67	34.14
6.6	1.49	44.91	2.69	36.83
5.3	25.7	70.61	2.97	39.80
4.2	4.23	74.84	2.11	41.91
3.3	8.36	83.20	1.48	43.39
2.6	3.52	86.72	1.11	44.50
2.1	2.76	89.48	1.36	45.86
1.7	1.80	91.28	2.98	48.84
1.3	1.89	93.17	15.81	64.65
1.0	1.61	94.78	18.54	83.19
0.83	3.85	98.63	10.48	93.67
0.66	1.38	100.00	6.33	100.00

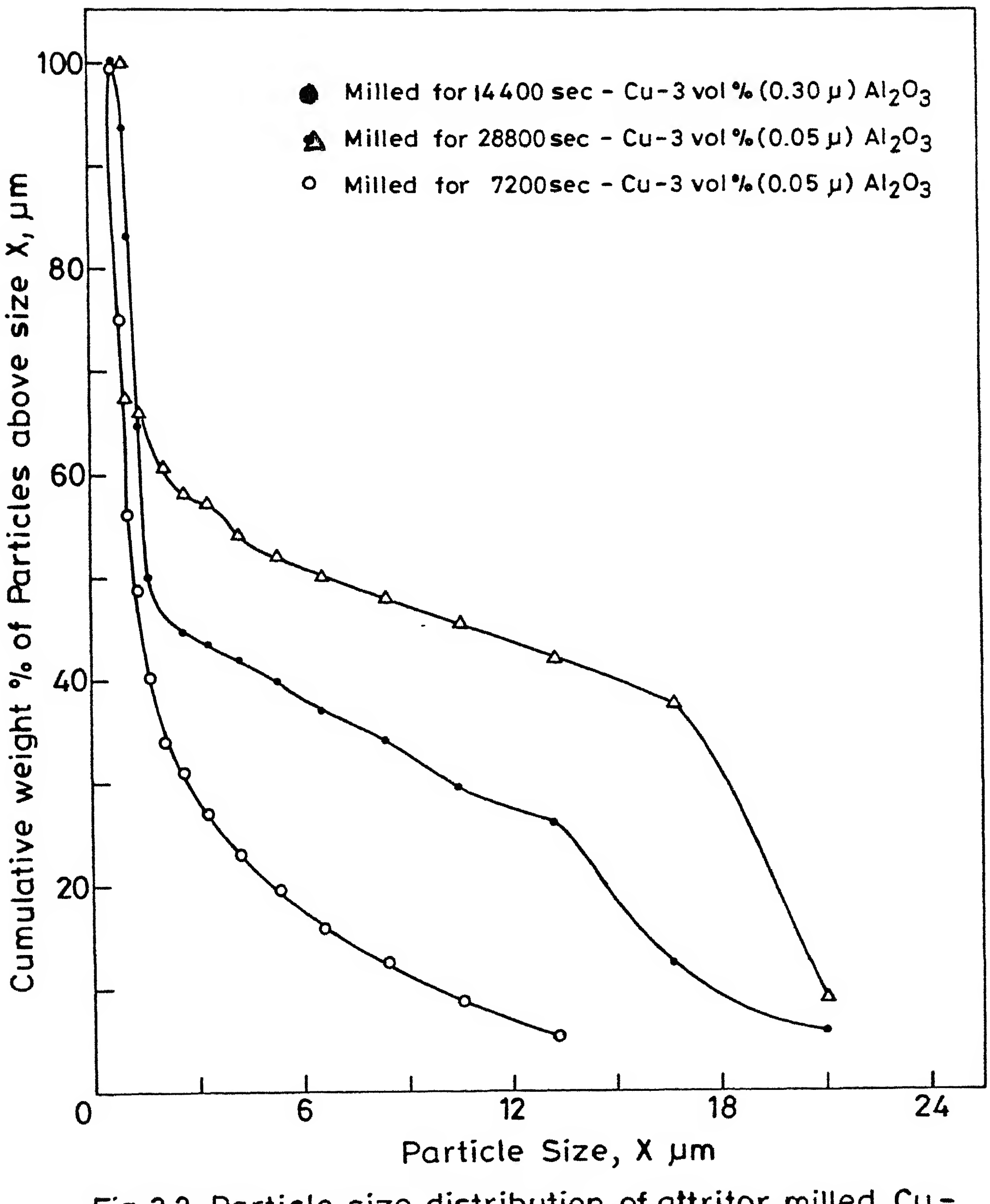

Fig. 3.2 Particle size distribution of attritor milled Cu-3 vol % Al_2O_3 powders determined by coulter counter method.

TABLE 3.2 : Size distribution of attritor milled Cu-3vol.Al_2O_3 powder determined by Coulter counter method

Average particle diameter in m	Time of attrition action					
	7,200 seconds		14,400 seconds		28,800 seconds	
	Weight %	Cumulative weight%	Weight%	Cumulative weight %	Weight%	Cumulative weight%
26.5	0	0	0	0	0	0
21.1	5.75	5.75	0	0	8.99	8.99
16.7	11.5	17.25	0	0	28.47	37.46
13.3	8.3	25.88	5.2	5.2	4.49	41.95
10.5	3.59	29.47	3.5	8.7	3.37	45.32
8.4	4.67	34.14	3.9	12.6	2.25	47.57
6.6	2.69	36.83	3.69	16.29	2.72	50.29
5.3	2.97	39.80	3.58	19.87	1.97	52.26
4.2	2.11	41.91	3.26	23.13	1.87	54.13
3.3	1.48	43.39	3.74	26.87	3.02	57.15
2.6	1.11	44.50	3.93	30.80	1.18	58.33
2.1	1.36	45.86	3.46	34.26	2.14	60.47
1.7	2.98	48.84	6.05	40.31	2.54	63.01
1.3	15.81	64.65	8.72	49.03	2.87	65.88
1.0	18.54	83.19	8.69	57.72	1.97	67.85
0.83	10.48	93.67	17.38	75.10	32.15	100.00
0.66	6.33	100.00	24.92	100.00	0.00	100.00

increases, the coarser size particles form. Moreover, the maximum coarse size particles obtained in 28,800s milling operation present in 7,200s milling operation particle size distribution for 14,400s milling operation is intermediate between that of 7,200s and 28,800s milling operation. From this figure, it can be seen that relative percentage of coarser particles is increasing with time of attritor milling operation due to predominant cold welding than fracturing of fine particles.

3.2 Preparation of Green Strips from Attritor Milled Cu-Al_2O_3 Powder by Bonded Powder Rolling Route:

Because of the lower apparent density (0.4 Mg/m^3) of attritor milled Cu-Al_2O_3 powder, it has found that green strip casted by Bonded Powder Method also had low apparent density (1.1 Mg/m^3). Densification of this porous Cu-Al_2O_3 strip sintering was difficult to attain either by repeated cold rolling and resintering cycle or by hot rolling. Even after compaction by using hydraulic press at the pressure of 130 MPa, the densification was not achieved because of lower density (3.6 Mg/m^3) of the Cu-Al_2O_3 compact. It was also observed that the Cu-Al_2O_3 strips easily cracked laterally and at edges during cold rolling operation, even for as low a reduction per pass as 5% and after 3 passes with intermediate annealing at 1123K for 1800s. Hot rolling of this green strip was difficult to carry out because of lower strength at high temperature.

Under these circumstances, it was decided to compact the $Cu-Al_2O_3$, powder in a die to get a preform and strips were made from these 'preforms'.

3.3 Preparation of Preform from Attritor Milled $Cu-Al_2O_3$ Powder by Die Compaction:

Die compaction of the $Cu-Al_2O_3$ powder was carried at a pressure of 160MPa. The apparent density of this die compacted $Cu-Al_2O_3$ preform was foundto be 4.5 Mg/m^3 which was approximately 50-55% of theoretical density. The dimensions of the preform was found to be 69 mm x 46 mm x 45 mm. It was observed that the cold rolling was not suitable to attain densification of this die compacted $Cu-Al_2O_3$ preform to strip form because of the cracking problem as observed in case of the cold rolling of $Cu-Al_2O_3$ preform which was prepared by bonded powder rolling method.

This problem led to the choice of hot rolling as densification step for forming this die compacted $Cu-Al_2O_3$ preform into strip, after sintering operation.

3.4 Sintering of the Die Compacted $Cu-Al_2O_3$ Preform:

It was found that the dimension of sintered $Cu-Al_2O_3$ preform was 58.4 mm x 39.5 mm x 5.4 mm. During sintering operation, it was found that blisters formed on the preform's surface and laminations were also observed along the outer thickness surfaces.

These blisters formed due to the faster diffusion of hydrogen gas into the preform to reduce cuprous oxide to copper. This typical problem is referred to as hydrogen embrittlement in powder rolling terminology and can be eliminated by reducing the rate of above reduction reaction. Blister problem has eliminated with adoption of two stage sintering operation which comprises of 1800s exposure to 773K initially and then 1800s exposure to 1123 finally.

3.5 Densification of Sintered $Cu-Al_2O_3$ Preform by Hot Rolling Route into Strip Form:

It was observed that hot rolling could not be carried out directly on sintered compact directly into a dense strip from the sintering furnace. Hot rolling was done on sintered $Cu-Al_2O_3$ preform after reheating it for 900s. In earlier studies on the hot rolling of sintered copper strips containing no oxide dispersion, it was possible to densify the strip by hot rolling in a single pass[43]. However, in the present investigation, it was observed that it was not possible to densify the $Cu-Al_2O_3$ preform into strip form by hot rolling in one single pass due to cracking of preform. This problem was over come by resorting to rolling in stages. The optimum hot rolling schedule was found to be 30-40% reduction per pass. It was found that total 90% thickness reduction was needed to get fully densify the preform into $Cu-Al_2O_3$ strip of 0.5-0.6 mm thickness. Typically, 6-7 passes were required to obtain a fully densified strip by hot rolling route.

Because the rolls of hot rolling mill were not heated externally, there was severe quenching of the Cu-Al_2O_3 strip on the surface during the last few passes and the hot rolling operation carried in these condition can be classified as warm rolling operation. To remove any quenching effect on the surface of the strips, the strips were annealed at 673 K for 1800s in N_2 atmosphere.

It was difficult to hot roll Cu-8 vol. % Al_2O_3 perform because of cracking problem even at 20% reduction per pass unlike Cu-3 vol. % Al_2O_3 strips.

3.6 Cold Rolling of Fully Densified Hot Rolled Cu-Al_2O_3 Strip:

Cold rolling of fully densified hot rolled Cu-Al_2O_3 strip was carried out upto an extent of 90% thickness reduction without any intermediate annealing. It was found that the strip behaved very well. There was no evidence of cracking.

3.7 Properties of Fully Densified Hot Rolled Cu-Al_2O_3 Strip

3.7.1 Variation of Density with Volume Fraction of Al_2O_3 in Cu-Al_2O_3 Strip:

Variation of density of fully densified hot rolled Cu-Al_2O_3 strip with volume fraction of Al_2O_3 can be seen in Fig. 3.3 and Table 3.3. The observed density values for 3 vol.% and 6 vol.% of Al_2O_3 in Cu-Al_2O_3 strips were in good agreement with theoretical density values. The slight variation of the observed value was due to experimental errors. Full densification of Cu-Al_2O_3 strip was achieved after 90% total reduction by hot rolling route.

3.7.2 Mechanical Properties of Fully Densified Hot Rolled Cu-Al_2O_3 Strips:

Strength properties obtained at room temperature of hot rolled Cu-Al_2O_3 strip are seen in Fig. 3.4 and Table 3.4 in both hot rolled and annealed condition. It can be seen from this figure that strength properties are higher for as hot rolled condition than annealed condition as expected. The variation of these strength values with volume fraction of Al_2O_3 in Cu-Al_2O_3 is unexpected because the increasing tendency can be seen from pure copper strip to the copper strips containing 3 vol.% Al_2O_3 (0.3μm size) and decreasing tendency can be observed from the strips containing 3 vol.% Al_2O_3 (0.3μm size) to the strips containing 6 vol.% Al_2O_3 (0.3μm size). However, the values corresponding to the strips containing 6 vol.% Al_2O_3 (0.3μm size) were higher than those of pure copper.

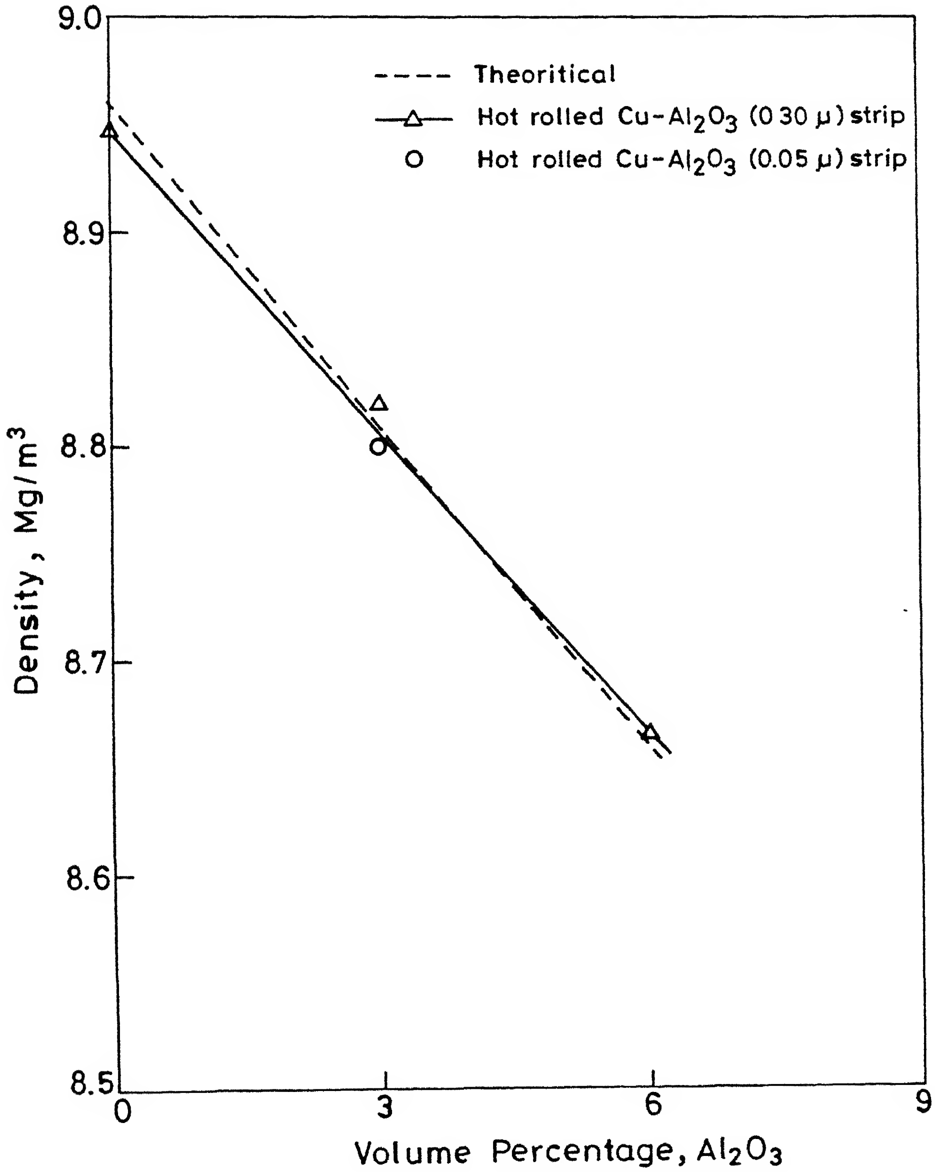

Fig. 3.3 Variation of density with volume fraction of Al_2O_3 in Cu-Al_2O_3 strip.

TABLE 3.3 : Variation of density with volume fraction of Al_2O_3 in $Cu-Al_2O_3$ strips

Material	Density, mg/m^3	
	Theoretical	Observed
Pure copper Al_2O_3	8.96	8.95
Cu-3vol.%(0.3 m size)	8.81	8.82
Cu-3vol.%(0.05 m size)	8.81	8.80
Cu-6vol.%(0.3 m size)	8.66	8.665

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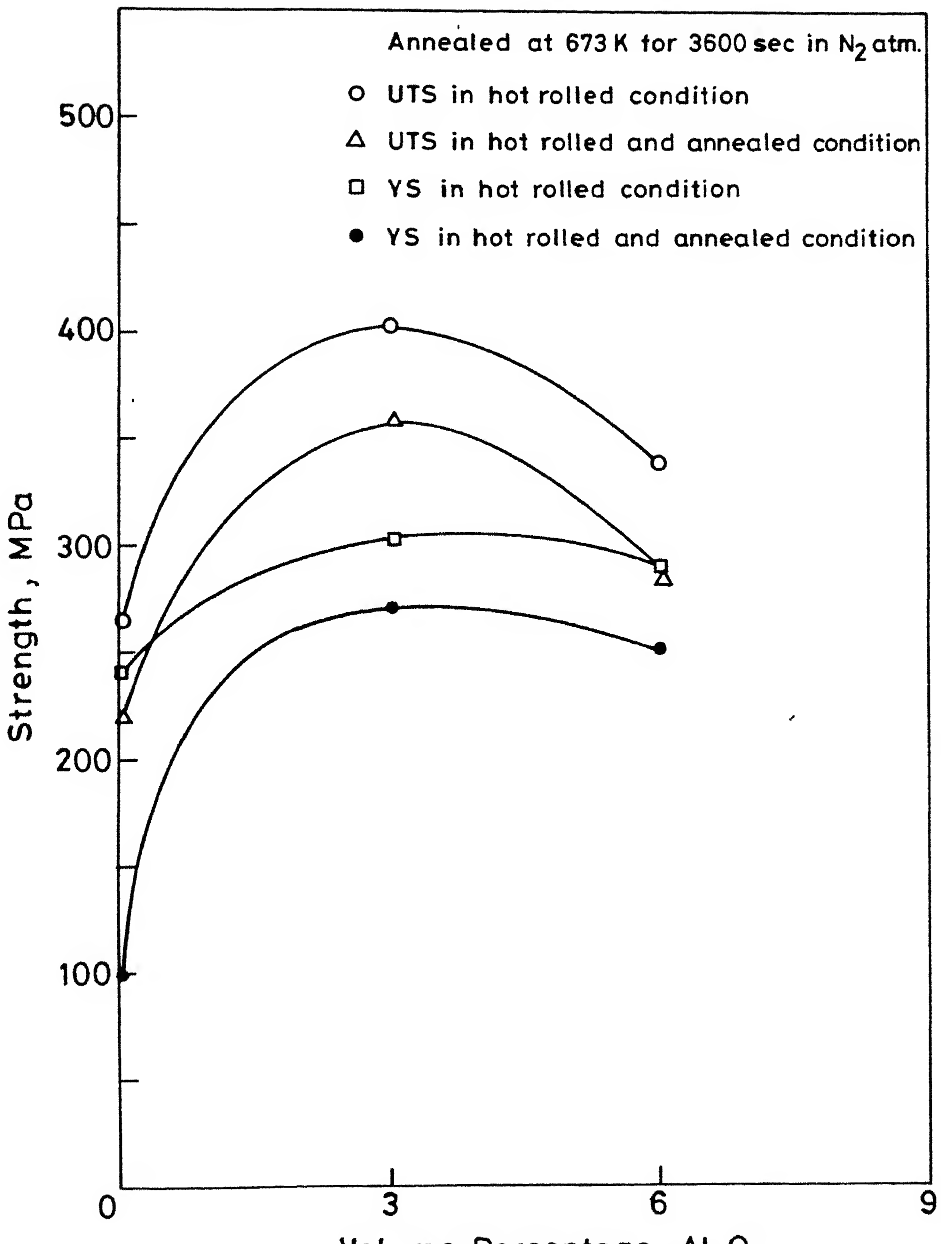


Fig. 3.4 Variation of YS and UTS of Cu-Al_2O_3 strip with volume fraction of Al_2O_3

TABLE 3.4 : Variation of properties of $Cu-N_2O_3$ strip with volume fraction of Al_2O_3

Material	Condition	Mechanical properties		
		0.2% offset yield stress, MPa	Ultimate tensile strength, MPa	Elongation, %
Pure copper	as hot rolled condition	220.6	265.1	11.5
Cu-3 vol.% Al_2O_3 (0.3 m size)	as hot rolled condition	360.4	403.3	6
Cu-6 vol.% Al_2O_3 (0.3 m size)	as hot rolled	257.3	340.2	6.5
Pure copper	hot rolled and annealed	99.2	242.8	36.5
Cu-3vol.% Al_2O_3 (0.3 m size)	hot rolled and annealed	265.4	307.8	10
Cu-6 vol.% Al_2O_3 (0.3 m size)	hot rolled and	255.8	287.5	9.8

Variation of % elongation with volume fraction of Al_2O_3 in Cu-Al_2O_3 strips is shown in Fig. 3.5 and Table 3.4 in both the conditions. It can be found from this figure, % elongation value is lower in as hot rolled condition than in annealed condition as expected due to quenching effect of rolls of hot rolling mill on the surface of the Cu-Al_2O_3 strips during last passes. Interestingly, % elongation does not vary from strips containing 3 vol.% to the strips containing 6 vol.% of Al_2O_3 (0.3 μm size) in both the above conditions.

From the above, it can be concluded that the strips containing 3 vol.% of Al_2O_3 (0.3 μm size) is giving optimum properties. When the properties of this strip are compared with those of the Cu-Al_2O_3 strip containing same vol.% of Al_2O_3 (0.05 μm size) as shown in Fig. 3.6 and Table 3.5, it can be seen that 0.2% offset yield stress and Ultimate tensile strength values are superior for the latter case. Moreover, the % elongation of the strip containing 3 vol.% Al_2O_3 (0.05 μm size) is slightly better than that of the strip containing 3 vol.% Al_2O_3 (0.3 μm size) which is the unexpected tendency. From this, it can be concluded that copper strip containing 3 vol.% Al_2O_3 (0.05 μm size) gives better combination of mechanical properties.

The effect of attritor milling time on mechanical properties of copper strips containing 3 vol.% Al_2O_3 (0.05 μm size) can be seen in Fig. 3.7 and Table 3.6. From this, it can be

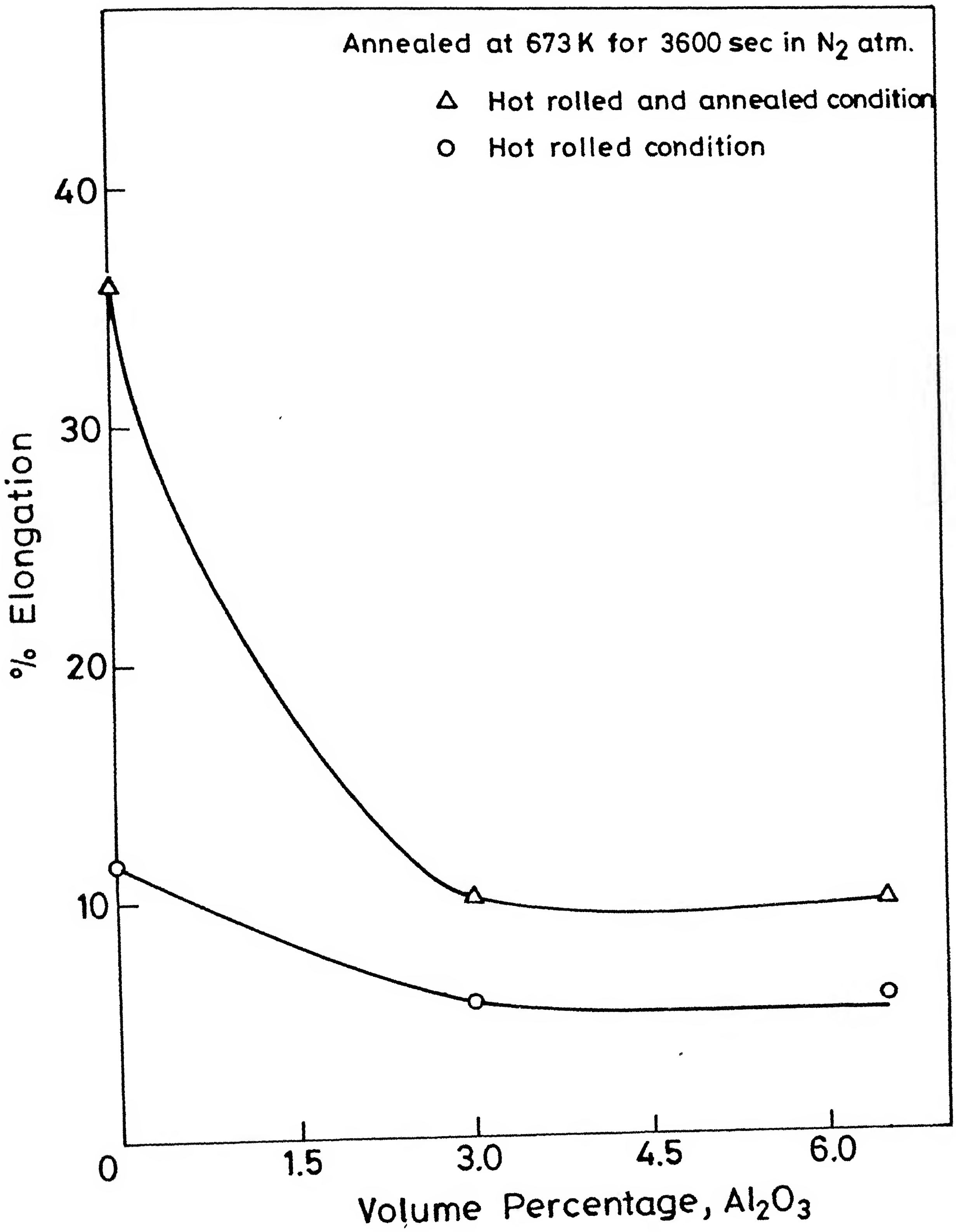


Fig. 3.5 Variation of % elongation of $Cu-Al_2O_3$ strip with volume fraction of Al_2O_3

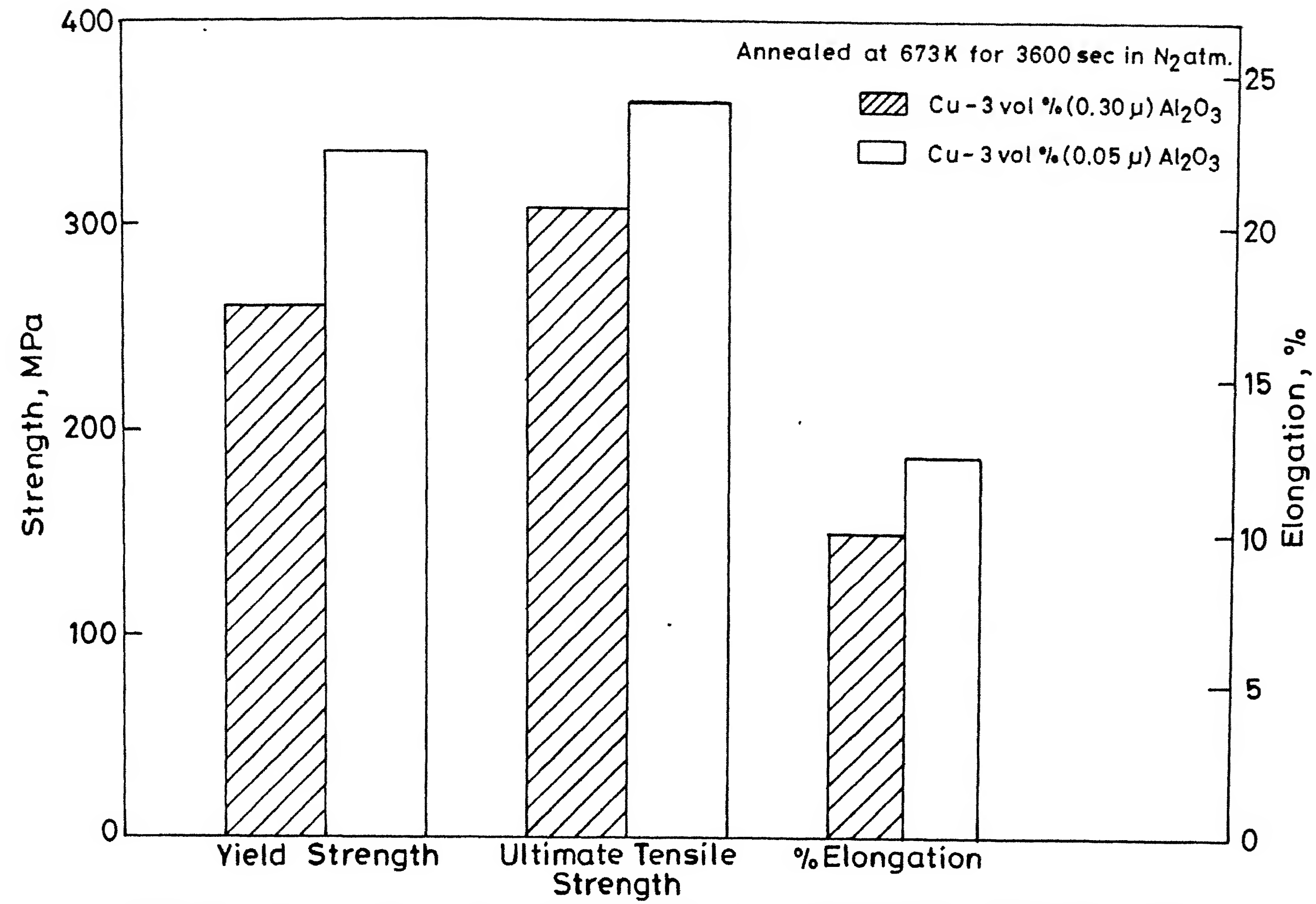


Fig. 3.6 Comparison of properties of Cu-3 vol % (with different size) strips in annealed condition.

TABLE 3.5 : Comparison of properties of Cu-3 vol.% Al_2O_3 (with different size) strips in annealed condition

Material	Condition	Mechanical properties		
		0.2% offset yield stress, MPa	Ultimate tensile stress, MPa	Elongation, %
Cu-3 vol.% Al_2O_3 (0.3 m size)	Hot rolled and annealed	265.4	307.8	10
Cu-3 vol.% Al_2O_3 (0.05 m size)	Hot rolled and annealed	335.2	360.3	12.5

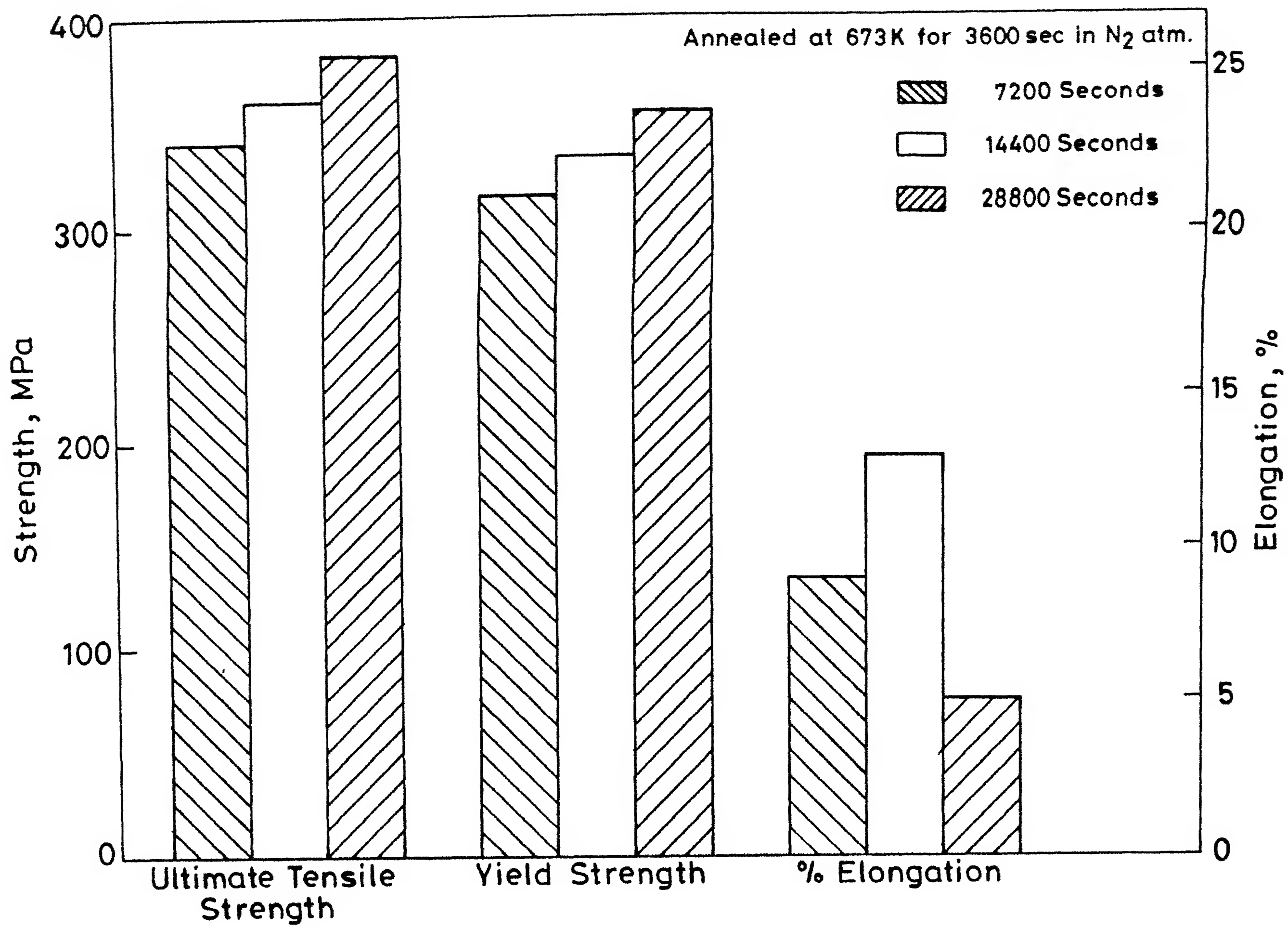


Fig. 3.7 Variation of properties of Cu-3vol % Al O (0.05 μm size) strips with milling time in altritor.

TABLE 3.6 L: Variation of properties of Cu-3 vol.% Al_2O_3 (0.05 μm size) strip with the milling time in attritor

Mechanical alloys time, sec.	Mechanical properties		
	0.2% offset yield stress, MPa	Ultrimate strength, MPa	Elongation, %
7,200	315.6	340.8	9.1
14,400	332.5	360.2	12.5
28,800	354.2	382.5	5.2

found that strength properties are increasing with attritor milling time. This trend is expected because of better distribution of Al_2O_3 in copper powder and work hardening effect on the powder. But % elongation value is varying unexpectedly with time of attritor milling and is difficult to explain. It can be seen from this figure that 14,400s time of attritor milling is giving optimum combination of mechanical behaviour.

At elevated temperatures, it is difficult to conduct experiments for measuring mechanical properties because of low thickness (0.44 mm) of samples after preparation from fully densified hot rolled $Cu-Al_2O_3$ strip having 0.55m thickness. The possible reason for this difficulty is due to self creeping of sample under supports weight in elevated temperature tensile testing conducted on Instron machine and combination of self creeping and oxidation of sample during heating in creep and stress rupture tests conducted in Satec System's creep machine.

3.9 Annealing Behaviour of Fully Densified Hot Rolled $Cu-Al_2O_3$ Strips After Cold Rolling:

The annealing behaviour of fully densified hot rolled $Cu-Al_2O_3$ strips after cold rolling can be correlated with mechanical behaviour at elevated temperature(6). To determine the annealing behaviour, it was decided to anneal the $Cu-Al_2O_3$ strips at temperatures of 473K, 673K, 873K, 1073K and 1273K for 3600s. The variation of hardness values of the pure copper strip and the copper strips containing varying volume % Al_2O_3 particles of

0.3 m and 0.05 m sizes with different annealing temperature is shown in Fig. 3.8 and Table 3.7. The trend of hardness values indicates the softening tendency of the individual $Cu-Al_2O_3$ strip. From this, it can be found that the decrease in hardness is slow unto 673K and is relatively fast above 673K temperatures. However, the hardness values are higher for $Cu-Al_2O_3$ strips even at 1273K temperature in comparison with pure copper which shows large softening behaviour. It can also be seen from this figure, that the softening behaviour of the copper strips containing 3 vol.% Al_2O_3 (0-05 μm size) is better than that of the copper strips containing 3 vol.% and 6 vol.% Al_2O_3 (0.3 μm size). More over, the hardness value of 90% cold rolled in comparison with 50% cold rolled copper - 3 vol.% Al_2O_3 (0.05 μm) is better even though there is no significant change in softening behaviour.

To verify the above trend in hardness values, the microstructure of different $Cu-Al_2O_3$ and pure copper strips after exposure to different annealing temperatures were observed under opticalmicroscope. The microstructure of as hot rolled fully densified $Cu-Al_2O_3$ strip was also observed in etched condition. The relevant photographs of as hot rolled and cold rolled annealed condition of $Cu-Al_2O_3$ strips can be found in Fig. 3.9 and Fig. 3.10 - Fig. 3.12 respectively. It can be seen from these photographs that the signs of recrystallization at 673K was found in Cu-3 vol.% Al_2O_3 (0.3 μm size) and Cu-6 vol.% Al_2O_3 (0.3 μm size) and was not found in Cu-3 vol.% Al_2O_3 (0.05 μm size). It can also observed that at 1273°K grain

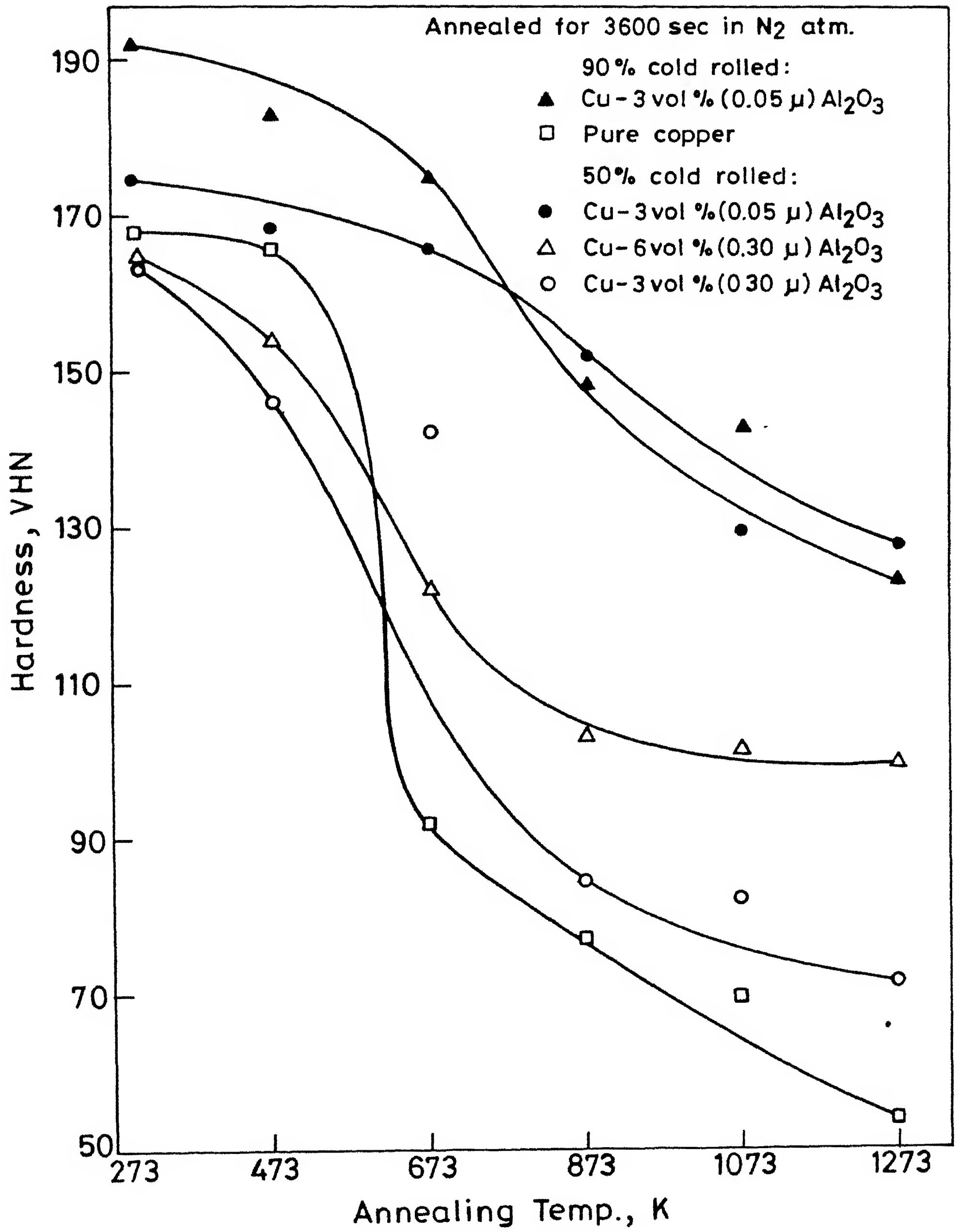
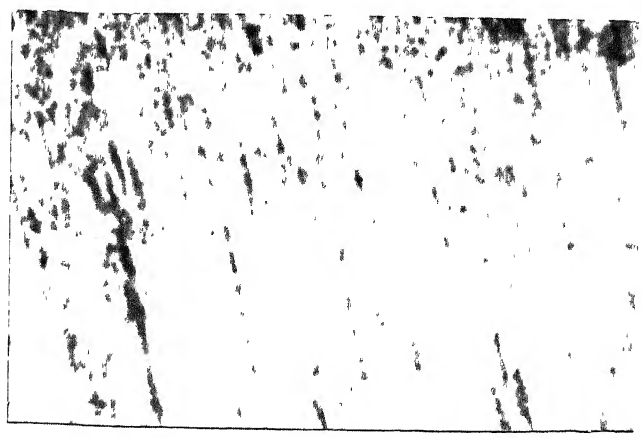


Fig. 3.8 Effect of annealing temperature on hardness of cold rolled pure copper and $Cu-Al_2O_3$ strips.

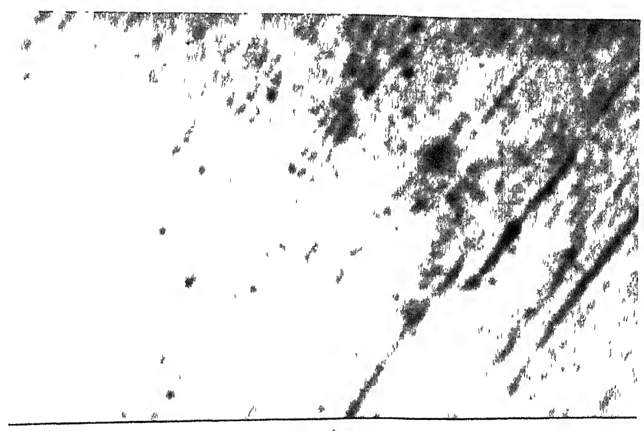
TABLE 3.7 : Effect of annealing temperature on hardness value (VHN) of cold rolled pure copper and Cu-Al_2O_3 strips

Material	Amount of cold rolling, %	Annealing temperature, K					
		300	473	673	873	1073	1273
Pure copper	90	168.0	166.0	91.8	77.0	69.6	53.6
Cu-3 vol.% (0.3μm Al_2O_3)	50	164.0	146.0	142.0	84.0	82.1	71.1
Cu-6 vol.% (0.3 μm Al_2O_3)	50	165.0	154.0	122.0	103.0	102.0	101.0
Cu-3 vol.%(0.05μm) Al_2O_3	50	175.0	168.0	166.0	152.0	129.0	128.0
Cu-3 vol.% (0.05μm) Al_2O_3)	90	192.0	183.0	175.0	148.0	143.0	123.0

(a)



(b)



(c)

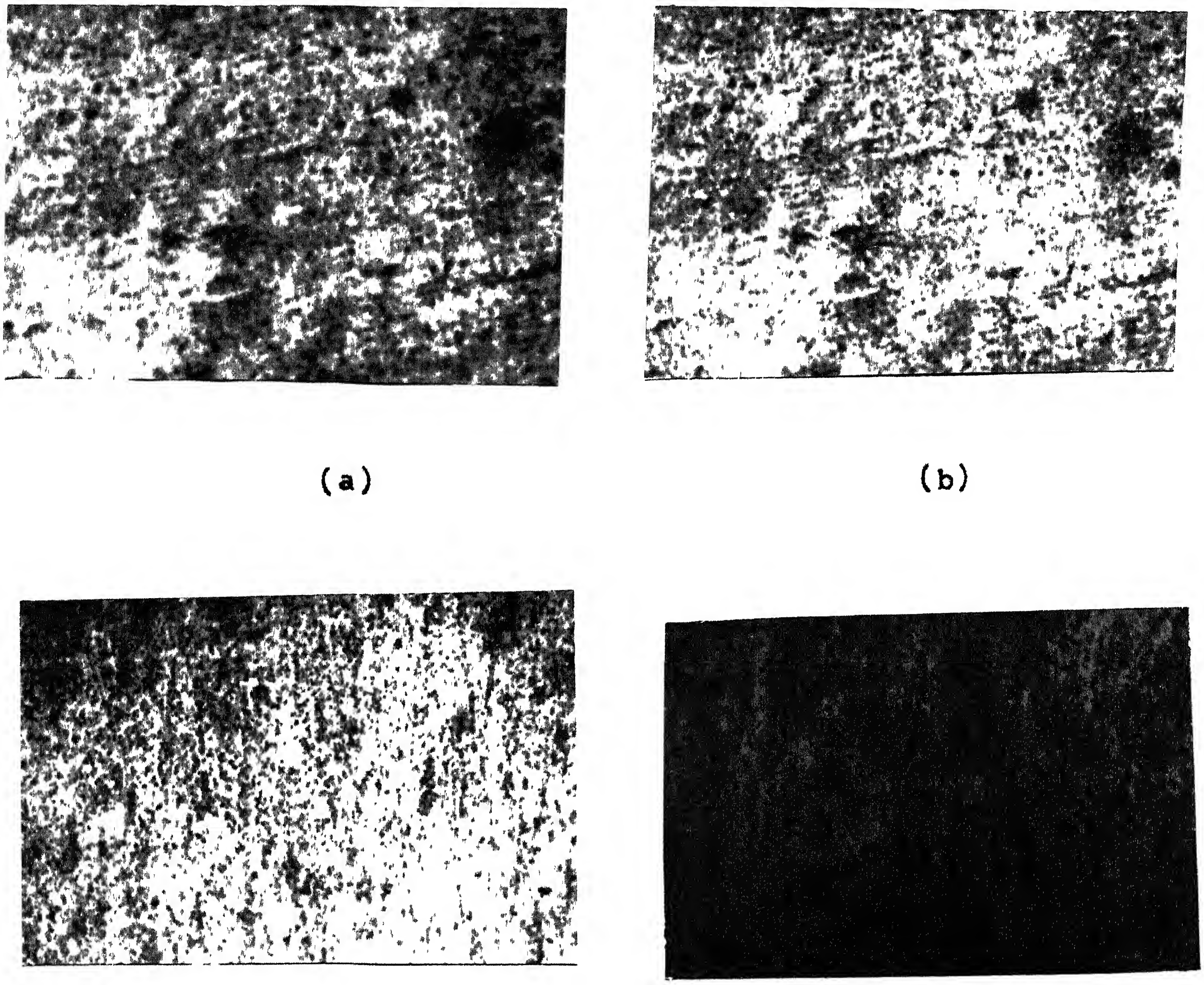
Magnification : 500 X

Fig. 3.9 : Optical micrographs of the fully Cu-Al_2O_3 strips obtained by hot rolling route, in etched condition

(a) Cu-3 Vol.%Al_2O_3 (0.3 μm size)

(b) Cu-6 vol.% Al_2O_3 (0.3 μm size)

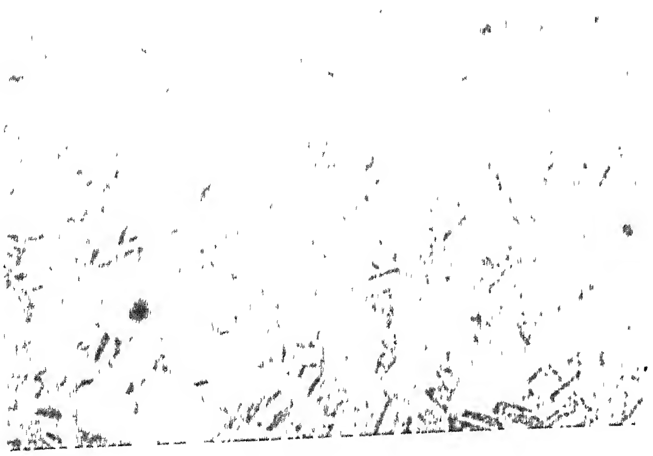
(c) Cu-3 vol.% Al_2O_3 (0.05 μm size).



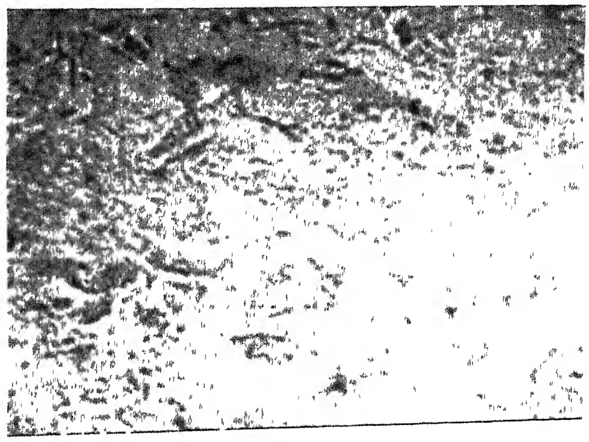
Magnification : 500 X

Fig. 3.10 : Optical micrographs of the fully dense pure copper and Cu-Al_2O_3 strips obtained by hot rolling - 50% cold rolling route

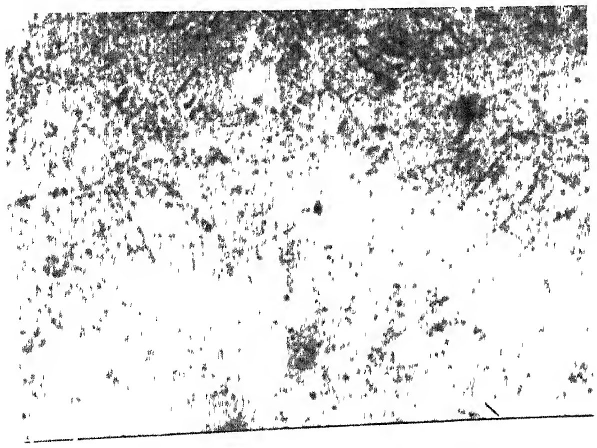
(a) Pure copper
(b) Cu-3 vol.% Al_2O_3 (0.3 m size)
(c) Cu-6 vol.% Al_2O_3 (0.3 m size)
(d) Cu-3 vol.% Al_2O_3 (0.05 m size)



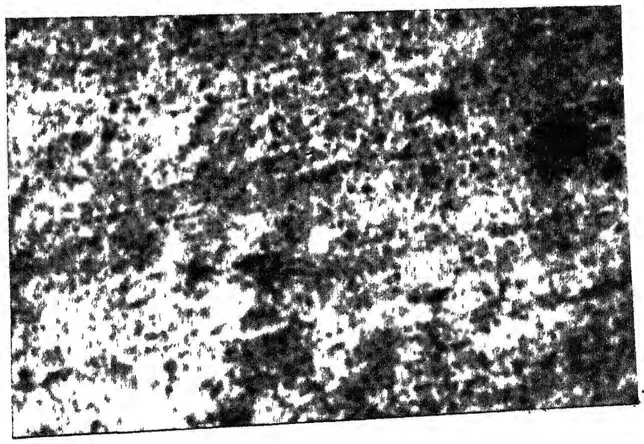
(a)



(b)



(c)

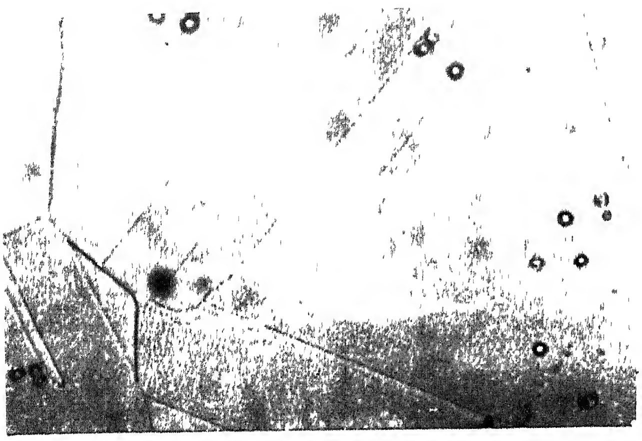


(d)

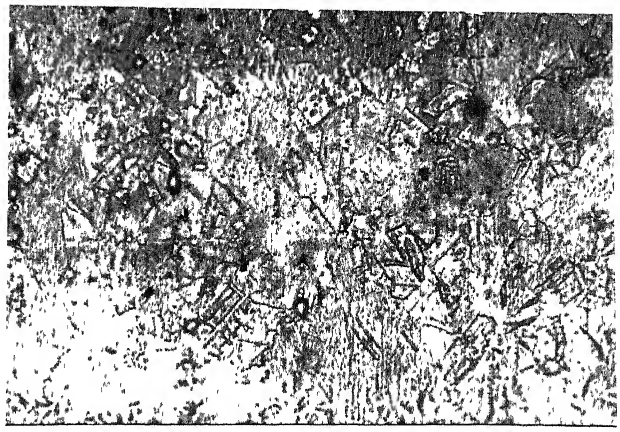
Magnification : 500 X

Fig. 3.11 : Optical micrographs of the annealed pure copper and Cu-Al_2O_3 strips obtained by hot rolling - 50% cold rolling route, at 673K for 3600 s.

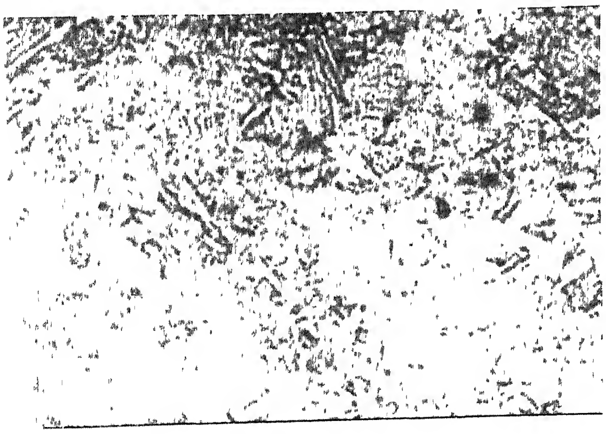
a) Pure copper;
b) Cu-3 vol.% Al_2O_3 (0.3μm size)
c) Cu-6 vol.% Al_2O_3 (0.3 μm size)
d) Cu-3 vol.% Al_2O_3 (0.05μm size)



(a)



(b)



(c)

(d)

Magnification : 500 X

Fig. 3.12 : Optical micrograph of annealed pure copper and $Cu-Al_2O_3$ strip obtained by hot rolling - 50% cold rolling route, at 1273K for 3600 s.

a) Pure copper
b) Cu-3 vol.% Al_2O_3 (0.3 μm size)
c) Cu-6 vol.% Al_2O_3 (0.3 μm size)
d) Cu-3 vol.% Al_2O_3 (0.05 μm size).

coarsening is significant in pure copper and is not so much is Cu-3 vol.% Al_2O_3 (0.05μm size) strip. These observations are in good agreement with the softening tendency observed by hardness measurements.

3.10 Comparison of Observed Properties with Those Available in Literature for Oxide Dispersed Copper Strips:

Densification of alumina dispersed copper powder by compaction and hot rolling route is in agreement with the observations made by other researchers[?,37,8,11,13]. The comparison of mechanical properties of fully densified hot rolled Cu-Al_2O_3 strips with those reference data from literature which correspond to cold extruded or cold rolled bar or strips after densification by hot working, can be seen in Fig. 3.13 and Table 3.8. From this, it is observed UTS of Cu-3 vol.% Al_2O_3 (0.05μm size) strip was between that of Cu-Al_2O_3 strip manufactured by mechanical mixing and by Internal Oxidation Methods. This value is comparable with that found is coprecipitation and spray drying methods. It can also be found that the % elongation of the Cu-3 vol.% Al_2O_3 strip obtained in this investigation was found to be similar to those of mechanical mixing and coprecipitation, but inferior to that of internal oxidation method.

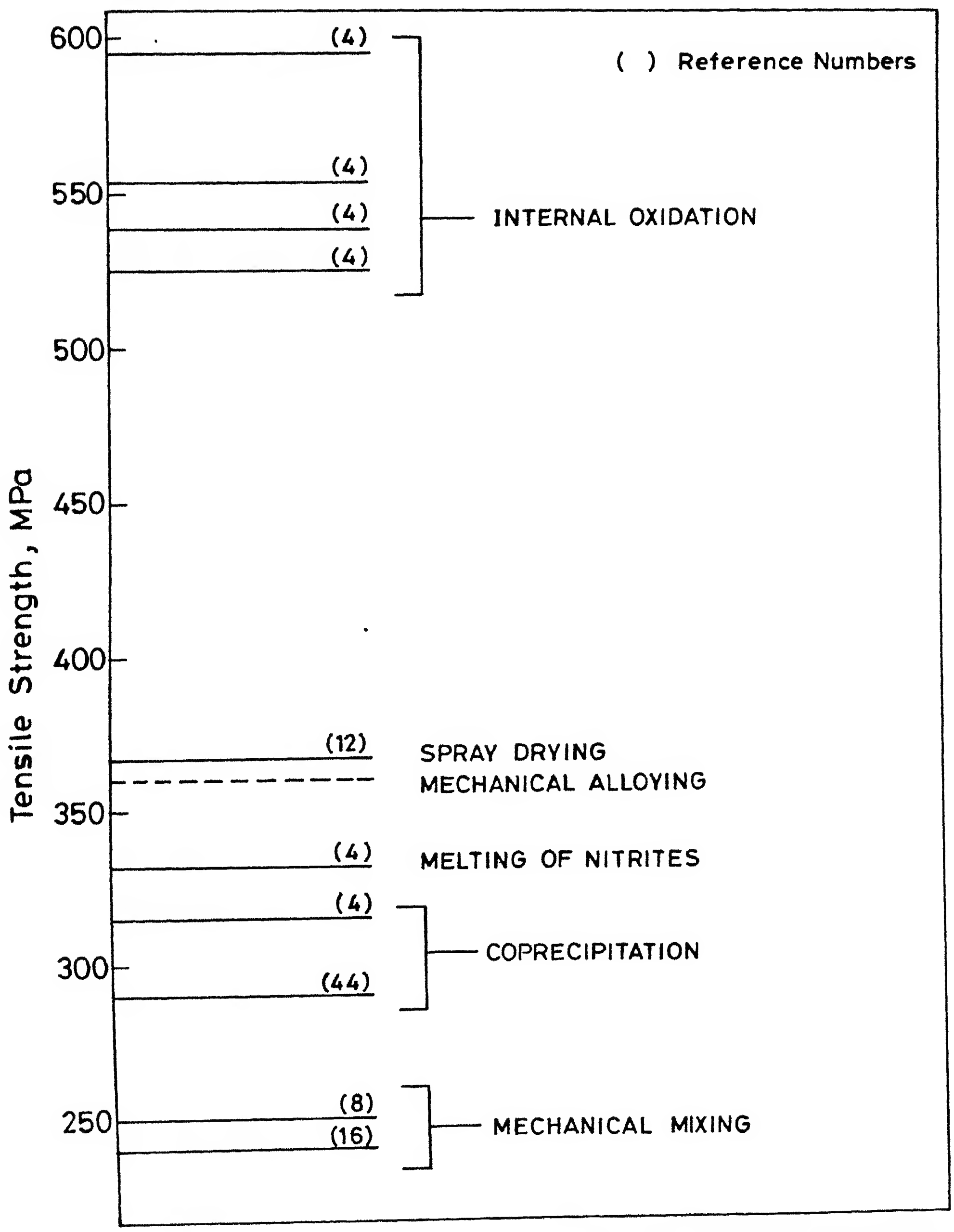


Fig. 3.13 Comparison of observed ultimate tensile strength value with those obtained by other methods of prepration of oxide dispersion strengthened (ODS) copper strips in annealed condition.

TABLE 3.8 : Comparison of observed mechanical properties with those obtained by other methods of preparation of ODS copper strips

Process	Vol.pct Al_2O_3	Copper/particle Size(μm)	Reduction ratio	0.2% offset Y.S.,MPa	UTA MPa	Elongation, %	Ref.
Mechanical mixing	2.5	74	20	180	230	15	(8)
Mechanical mixing	2.5	1	20	190	250	20	(17)
Mechanical mixing	3.0	45	13	190	250	13	(8)
Coprecipitation	2	-	16	300	335	12	(8)
Coprecipitation	3	-	16	325	395	16	(8)
Internal oxidation	0.4	10-100	30	380	470	24	(8)
Internal oxidation	1.4	10-100	30	460	520	18	(4)
Spray drying	1.0 vol.% ThO_2	-	9 (by not rolling)	151	261	17.7	(16)
Mechanical alloying	3 vol.%	12	9 (by not rolling)	335.2	360.3	12.5	Own

The observed softening behaviour of Cu-Al_2O_3 strip with those obtained from literature[2,7,4,8,13] can be seen in Fig.3.14 and Table 3.9. Data collected from literature was for 90% cold worked oxide dispersed copper strips and were compared with 50% cold worked Cu-Al_2O_3 strip obtained in this investigation. The softening of annealing behaviour observed in prepared Cu-Al_2O_3 strips is similar to behaviou found in other oxide dispersed copper strips, which can be seen from the Fig. 3.14.

3.10 Discussion

From the above results, it can be deduced that the ductile nature of copper powder lead to the formation of coarser particles during attritor milling which involves competitive cold welding and fracturing processes. The Cu-Al_2O_3 powder after attritor milling has relatively finer particles in comparison with copper powder due to its lower ductility. From this studies, it seems that the particle size distribution of Cu-Al_2O_3 powder also depends on the time of attritor milling. As the time of milling increases, particles are becoming coarser in general, but still the average particle size is much smaller than the original average size of the copper powder. It seems that the competition between cold welding and fracturing determines the size of the resulting powder. The saturated size distribution of Cu-Al_2O_3 powder has not been achieved during this investigation.

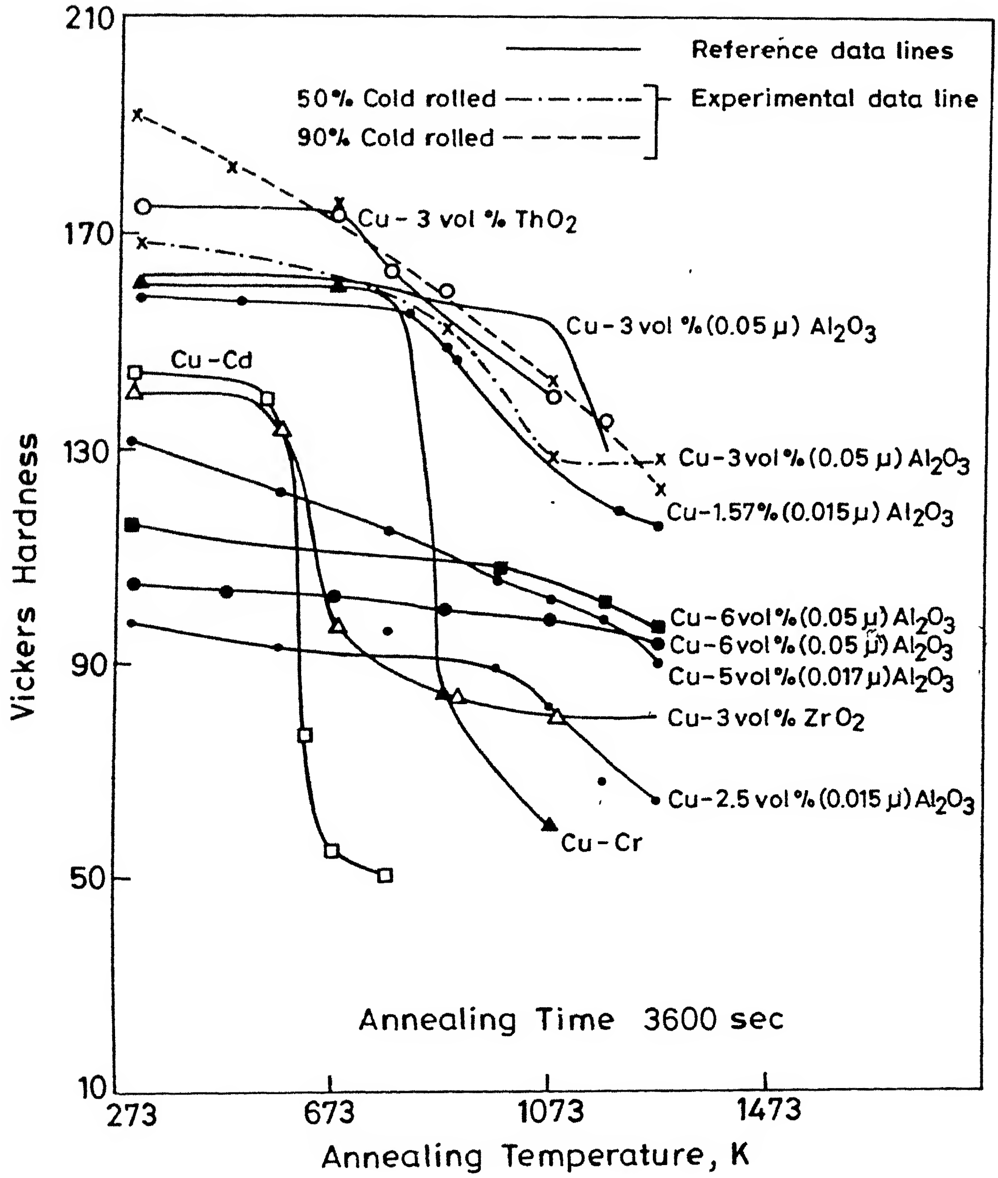


Fig. 3.14 Comparison of observed annealing trend with those found by other methods in oxide dispersion strengthened (ODS) copper strips.

TABLE 3.9 : **Comparison of observed annealing trend in this investigation with those found by other methods of preparation of ODS copper strips**

Material	Method of preparation	Hardness value in VHN after annealed for 3,600 s time (annealing temperature, K)							Ref.
Cu-Cd	Precipitation hardening	138 (300)	137.5 (373)	137 (523)	130 (573)	59 (673)	56 (773)		2
Cu-Cr	Precipitation hardening	160 (300)	160 (373)	159.5 (523)	159.0 (673)	158.5 (700)	140 (773)		2
Cu-3 vol.% Al_2O_3 (0.03 μm size)	Mechanical mixing	104 (300)	103.5 (473)	103 (673)	101 (873)	100 (1073)	96 (1273)		22 2
Cu-5 vol.% Al_2O_3 (0.03 μm size)	Mechanical mixing	112 (300)	110 (473)	109 (673)	108 (873)	106 (1073)	102 (1273)		2
Cu-3 vol.% ThO_2 (0.05 μm size)	Precipitation press	170 (300)	170 (673)	165 (773)	150 (973)	124 (1173)			7
Cu-2.5 vol.% ZrO_2 (0.15 μm size)	Precipitation press	150 (300)	150 (473)	132 (573)	90 (673)	82 (873)	81 (973)	80 (1073)	7
Cu-1.57 vol.% Al_2O_3 (0.01 μm size)	Internal oxidation	158.7 (300)	157.3 (500)	153.3 (700)	151.4 (900)	150.7 (1200)	116 (1273)		4
Cu-3.0 vol.% Al_2O_3 (0.05 μm size)	Mechanical mixing	161.3 (300)	160 (473)	158.7 (673)	156 (873)	153.3 (1073)	130 (1273)		8

Continued

TABLE 3.9 (Continued):

Material	Method of preparation	Hardness value in VHN after annealed for 3,600 s time (annealing temperature, K)							Ref.
Cu-2.5 vol.% Al_2O_3 (0.018 m size)	Mechanical mixing	98 (300)	96 (573)	93 (773)	96 (973)	89 (1073)	68 (1175)	64.5 (1273)	16
Cu-5.0% vol.% Al_2O_3 (0.018 m Al_2O_3)	Mechanical mixing	131 (300)	122 (573)	114.7 (773)	11087 (973)	10287 (1073)	192.5 (1173)	97.5	16
Cu-3 vol.% Al_2O_3 (0.05 m size) For 50 cold rolled	Mechanical alloying	175 (300)	168 (473)	166 (673)	152 (873)	129 (1073)	128 (1273)		own
For 90 cold rolled	Mechanical allowing	192 (300)	183 (473)	148 (673)	148 (873)	143 (1073)	123 (1273)		own

The poor cold rolling behaviour of the porous Cu-Al_2O_3 preform is due to incoherent interface between Al_2O_3 and copper, presence of considerable amount of porosity and poor densification during sintering treatment. The possibility of presence of some Al_2O_3 particles along the grain boundaries will also increase the tendency of cracking. This problem was not experienced during Hot rolling of Cu-Al_2O_3 preform into strip form because of increased ductile nature of copper at such working temperature of 1123K.

The decreasing tendency of mechanical properties at room temperature from the strips containing 3 vol.% Al_2O_3 (0.3 m size) to the strips containing 6 vol.% Al_2O_3 (0.3 m size) is possible due to more amount of Al_2O_3 in the latter due to the formation of agglomerates. The probable reason for better mechanical properties of the strips containing 3 vol.% Al_2O_3 (0.05 m size) in comparison with those of the strips containing same volume % of Al_2O_3 with 0.3 m size is due to finer size of Al_2O_3 so that better strengthening can be resulted because of relatively lower interparticle spacing which increases the strength properties. The improvement of mechanical properties of Cu-Al_2O_3 strip with the time of attritor milling is due to better distribution of Al_2O_3 in copper powder.

The difficulty in conducting the elevated tensile testing, creep testing and stress rupture testing is due to the smaller thickness of the samples used and can be overcome by using thicker sample. Because of minimised self creeping of the sample under

the weight of supports used to grip it; it can be possible to conduct the above tests to evaluate the mechanical behaviour at elevated temperatures. The use of protective atmosphere during the above tests will definitely improve the capability of conducting the above tests. Conducting the tests at temperatures lower than 873K will not give good correlated service performance results.

The qualitative method of measuring the mechanical or softening behaviour is comprises of subjecting the samples of $Cu-Al_2O_3$ strips to annealing treatment for 3600s at different temperatures and measuring the hardness value. This method has also been used by other researchers(2,4,7,8) to correlate the softening behaviour with hardness values. For a better correlation of this behaviour, the annealing treatment may be conducted for longer periods of time, say 10-50 hours. From the results obtained, it can be seen that softening starts at 673K for the $Cu-Al_2O_3$ strips, and Cu-3 vol.% Al_2O_3 (0.05 m size) strip gives better properties. Even though, the softening behaviour for such a short period has been investigated, the same results can be expected for larger periods of time because of lower rate of coarsening of Al_2O_3 in copper due to insolubility. The hardness values obtained in this investigation, are superior to those found in $Cu-Al_2O_3$ bars produced by mechanical mixing - Hot and cold extrusion route(2,17) even at annealing temperature

of 1273K and are comparable with those obtained in Cu-ThO_2 and ZrO_2 strips produced by reverse gel process and subjected to extrusion[7].

The above trend can be noticed from Fig. 3.14 and Table 3.14. The tendency of softening was also observed through recrystallization nature of microstructure by optical metallography and was found to be in good correlation with observed hardness values. The higher softening tendency in Cu-3Al_2O_3 (0.3 m size) and Cu-6 vol.%Al_2O_3 (0.3 m size) may be possibly due to larger interparticle spacing in the former, and agglomerated cluster formation in the latter. It is interesting to notice that the results obtained in the present investigation even is hot rolled condition are superior than those obtained by using mechanical mixing technique for preparation of Al_2O_3 dispersed copper powder, followed by hot and cold extrusion and are comparable with those using coprecipitation and spray drying methods for powder preparation and hot extrusion for consolidation followed by cold rolling. By subjecting the prepared hot rolled Cu-Al_2O_3 strips to cold rolling it is possible to improve the mechanical properties at room temperature.

It is also interesting to notice that the softening behaviour of cold rolled Cu-3vol.% Al_2O_3 (0.05 m size) made in the present work is superior in comparison of Cu-Al_2O_3

strips produced by mechanical mixing - hot and cold extrusion routes and is comparable with that observed in oxide dispersed copper produced by reverse gel method - hot extrusion - cold rolling route. The decrease in hardness values observed in cold rolled Cu-3 vol.% Al_2O_3 (0.05 m size) strip with annealing temperature is relatively more than that observed in other methods of preparing oxide dispersed copper involving hot extrusion for consolidation. The reason for this is difficult to explain because of limited knowledge of mechanical and structural behaviour of ODS copper.

CHAPTER 4

CONCLUSIONS

4.1 Conclusions

(1) The present investigation shows that attritor milled Cu-Al_2O_3 is finer than the starting copper powder. The powder size increases with the time of milling, used in present investigation. However the powder size even after milling for 28,800s is finer than the original copper powder size.

(2) Hot rolling has been found to be a better technique for the densification of Cu-Al_2O_3 preform than the repeated cold rolling - resintering technique, because of problem of cracking in the latter.

(3) The cold rolling behaviour of fully densified hot rolled Cu-Al_2O_3 strip is good so that 90% total thickness reduction can be given without any intermediate annealing treatment.

(4) Copper strips containing 3 vol.% Al_2O_3 (0.05 m size) has been found to be the best amongst the materials investigated in the present study, and has the following mechanical properties at room temperature in annealed condition: (i) Yield Strength: 330 MPa; (ii) Ultimate Tensile Strength: 360 MPa and (iii) % Elongation : 12. It is also found that these properties of

$Cu-Al_2O_3$ strip even in hot rolled condition are superior in comparison with those of $Cu-Al_2O_3$ strips made by mechanical mixing of powders - Hot extrusion extrusion and cold rolling route and are comparable with those of oxide dispersed copper made by coprecipitation or spray drying method. Hot extrusion cold rolling route.

(5) The softening tendency of the Cu-3 vol.% Al_2O_3 (0.05 m size) is better than the other copper strips containing 3 vol.% and 6 vol.% Al_2O_3 (0.3 m size). It is superior than that found in $Cu-Al_2O_3$ strip made by mechanical mixing method, and is comparable with that found in oxide dispersed copper strip made by reverse gel process.

(6) Attritor milling for 14,400s has been found to be optimum for the Cu-3 vol.% Al_2O_3 (0.05 m size) strip because of better combination of mechanical properties when compared with those of 7,200s and 28,800s milling.

4.2 <u>Suggestions for Future Work</u>

(1) In the present work, the distribution of Al_2O_3 in copper strips has not been investigated. Further investigation should be carried out to analyse the Al_2O_3 particle distribution using electron microscopy.

(2) Densification behaviour of Cu-3 vol.% Al_2O_3 (0.05 m) strip during hot rolling should be investigated.

(3) Thicker fully densified Cu-3 vol.% Al_2O_3 (0.05 m size) strip by hot rolling should be made to further investigate the

mechanical behaviour at elevated temperatures.

(4) The anisotropy of mechanical properties should be investigated for strips of Cu-3 vol.% Al_2O_3 (0.05 m size) made by hot rolling followed by cold rolling.

(5) Measurement of electrical and thermal conductivities for Cu-Al_2O_3 strips should be done with variation of size and volume fraction of Al_2O_3 dispersed in copper.

(6) Mechanical alloying of Cu-Cd or Cu-Cd-Cr alloys with Al_2O_3 particles to make ODS copper alloys should be tried to further exploit the benefits of oxide dispersion strengthening to meet the critical requirements.

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